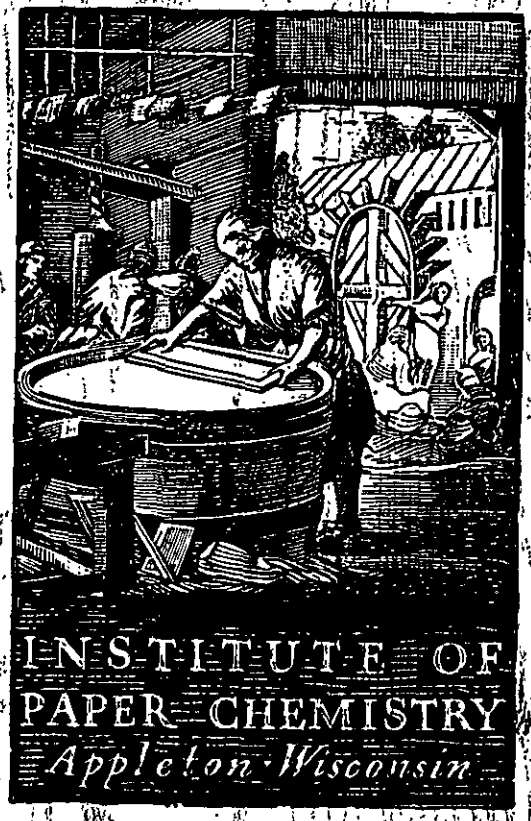

Institute of Paper Science and Technology
Central Files

SELECTIVE DELIGNIFICATION OF WOOD AND OTHER FIBROUS MATERIALS

CHLORINE DIOXIDE-ALKALI PULPS FROM ASPEN

Research Grant

Project 2500

Report Eight

A Progress Report

to

THE GRANTORS

June 6, 1969

THE INSTITUTE OF PAPER CHEMISTRY
Appleton, Wisconsin

Institute of Paper Science and Technology
Central Files

SELECTIVE DELIGNIFICATION OF WOOD AND OTHER FIBROUS MATERIALS

CHLORINE DIOXIDE-ALKALI PULPS FROM ASPEN

Research Grant

Project 2500

Report Eight

A Progress Report

to

THE GRANTORS

June 6, 1969

TABLE OF CONTENTS

THE INSTITUTE OF PAPER CHEMISTRY
Appleton, Wisconsin

SELECTIVE DELIGNIFICATION OF WOOD AND OTHER FIBROUS MATERIALS

CHLORINE DIOXIDE-ALKALI PULPS FROM ASPEN

SUMMARY

This report deals with the oxidative pulping of aspen using a sequence of steps that includes chip fiberization, alkali conditioning, oxidative reaction, alkali extraction, and hypochlorite reaction.

In chlorine dioxide-alkali pulping with alkali conditioning, by varying the alkali extraction time and hypochlorite reaction conditions, it has been shown that pulps with higher Canadian freeness are obtained not only when shorter extraction times are used but also when less hypochlorite is present. Prepared pulps included one made with a 10-min. alkali extraction time followed by reaction with 1.5% hypochlorite as well as another pulp made with a 120-min. alkali extraction time followed by reaction with 4.5% hypochlorite. While handsheet data revealed significant differences between these extremes the freeness values and densities encompassed only the lower freeness and higher density ranges covered by handsheets of a kraft reference pulp. Alkali extraction at 60°C. is recognized as functioning to rapidly remove modified lignin, and through extension of time to cause both a further liberation of fibers and an apparently contrary shift in fiber properties.

In chlorine dioxide-alkali pulping without alkali conditioning, by varying the alkali extraction with respect to time and amount of alkali, after reaction with hypochlorite total yields were 76-66% with about 18 to 4% screen rejects. Excessive screen rejects at a yield below the fiber liberation point are regarded as indicative of a nonuniform oxidative reaction within the coarser fraction of the fiberized chips. The group of pulps prepared without alkali conditioning showed a trend toward reduced sensitivity to beating when alkali

extraction conditions were milder, with the result that beating and handsheet data, respectively, showed freenesses and densities closer to those of a kraft reference pulp than obtained previously. It appears that opacity is lowered when alkali concentration is higher during extraction of modified lignin, and that lessening the extent of exposure to alkali is associated with a desirable shift in other fiber properties.

Comparison of chlorine dioxide-alkali pulps with and without alkali conditioning has been made on two pairs of pulps having a within-pair difference based on whether or not alkali conditioning preceded oxidative reaction and a between-pair difference concerned with time of extraction. As partly anticipated above, the time for beating to a particular freeness was longer for shorter extraction time on a between-pair basis of comparison. Within-pair and between-pair factors both apparently influenced TAPPI handsheet density, the lowest density occurring for no alkali conditioning coupled with shorter extraction time. Breaking length was better with omission of alkali conditioning. Zero-span breaking length and M.I.T. fold data were better without alkali conditioning and in addition it was concluded that one pulp, obtained in 63% yield, had been degraded. The parameters of alkali conditioning and alkali extraction both are concluded to significantly influence fiber properties on the basis of handsheet data.

Comparison of gaseous and aqueous chlorine dioxide-alkali pulps with and without alkali conditioning has been made on two pairs of pulps having roughly similar within-pair yields, lignin contents, freenesses, and brightnesses. The most notable differences in handsheet data were for the pair of pulps produced without alkali conditioning and concerned tear factor plus breaking length. Such differences could have arisen from the use of different lots of chips. Otherwise,

it was tentatively concluded the oxidative reaction can be carried out either by using gaseous or aqueous chlorine dioxide to give pulps with about the same properties.

By comparing all of the handsheet data for chlorine dioxide-alkali pulps it has been demonstrated that the tendency of holocellulose-type pulps to beat rapidly to low freeness with the provision of glassine-type handsheets is avoidable by changes in the pulping procedure.

Small, raised specks were often observed on the backs of handsheets from chlorine dioxide-alkali pulps. Caliper measurement studies of such sheets using the TAPPI method and mercury pycnometric density approach revealed the relationship between TAPPI sheet thicknesses and mercury sheet thicknesses for the handsheets from chlorine dioxide-alkali pulps failed to coincide with the same relationship for kraft reference pulp handsheets. Apparently, surface roughness causes variation in "intermeshing" of handsheets from the former pulps so that the TAPPI method does not form a satisfactory basis for determining handsheet density for direct comparison with kraft pulp handsheets. After taking this into account it was concluded the chlorine dioxide-alkali pulp properties can compare well with kraft except at lowest handsheet density.

Data on the hydrodynamic properties of some chlorine dioxide-alkali pulps are presented. The curve for Canadian freeness versus average drainage resistance of these pulps when compared with the curve for kraft pulps revealed a lower freeness at constant drainage resistance. When compressibility, specific volume, and specific surface were taken into account the hydrodynamic properties of chlorine dioxide-alkali aspen pulps approach those of kraft aspen pulps.

GENERAL INTRODUCTION

In the comprehensive review given in Report Six, reference was made to holopulp being prepared by a process with three essential features, namely:

(1) fiberization of chips,

(2) modification of lignin by an oxidant, and

(3) removal of modified lignin by alkali.

As this project has progressed, review has called for some revision of ideas through recognizing that the function of alkali extends beyond the removal of modified lignin. The significance of this is more apparent when a broader view is taken so as to encompass not only selective delignification but also other factors related to possibly achieving a viable pulping process.

In this report recognition will be given to some apparent functions of alkali through the use of a terminology that elaborates on the three essential features noted above.

For wood chips the steps of chlorine dioxide-alkali pulping may include:

(1) fiberization of chips,

(2) alkali conditioning,

(3) oxidative reaction to modify lignin,

(4) alkali extraction to remove modified lignin, and

(5) defibration by chemical or mechanical means.

Here, defibration is considered primarily within the limits of what can be achieved in the way of fiber liberation by a single hypochlorite treatment which also bleaches and reduces the lignin content of the pulp obtained. With this limitation particular attention has been given to learning more about the potential versatility

of this kind of pulping process, especially in terms of the types of pulp capable of being produced at a yield of not less than 65%.

CHLORINE DIOXIDE-ALKALI PULPING WITH ALKALI CONDITIONING

DISCUSSION

Introductory Comment

In Report Six, some handsheet data for unbleached Pulps LL-10, LL-60, and LL-240 were recorded in Table X, page 47. Before beating, these pulps had Canadian freeness values of 560, 565, and 515, respectively, and there was some indication that alkali extraction for 10 min. (Pulp LL-10) compared with 240 min. (Pulp LL-240) was associated with a trend toward greater handsheet density for equal beating times. However, the handsheet data for the pulps were generally similar, and no particular conclusion was drawn concerning any significant relationship of alkali treatment to handsheet properties. Screen rejects of 7.0, 2.8, and 2.0 for Pulps LL-10, LL-60, and LL-240 reflected the fact that the yield of LL-10 was above the defibration point.

After exploratory bleaching experiments as in Report Six, Table XX, page 76, to obtain sufficient pulp for preparing handsheets about equal amounts of Pulps LL-60 and LL-240 were combined. When bleached, the product was unusual in that the relatively unbeaten bleached pulp was more like the corresponding unbleached pulps after beating with respect to freeness, sheet density, and breaking length, for example. Examination of the data on the exploratory bleaching experiments seemed to indicate a significant factor in freeness, after bleaching with hypochlorite, could be the total time of alkali extraction, as well as the amount of hypochlorite applied when bleaching. If this indication were to be real, the observed trend would be relevant to the desire of achieving bleached pulps with higher initial freeness. Thus, the direction of further experiments was naturally established.

Varying Alkali Extraction and Hypochlorite Reaction

Using the methods described in the experimental part, alkali conditioned fiberized chips were subjected to oxidative reaction with 9.0% chlorine dioxide, then four portions were alkali extracted for 10, 30, 60, and 120 min. before each was reacted with different amounts of hypochlorite. The results of these experiments, along with relevant conditions, are presented in Table I, from which the curves in Fig. 1 have been derived. These curves illustrate that, while there is a linear relationship for the aged GE brightness versus the alkali extraction time (t) curves which have a similar slope for reaction with the equivalent to 1.5, 3.0, and 4.5% available chlorine, there is a nonlinear relationship for the three Canadian freeness (CF) versus the extraction time curves. For each of these curves, $-dCF/dt$ is greater as $t \rightarrow 0$; and for any given time $-dCF/dt$ is greater with increase in the amount of hypochlorite added.

In view of the observation that hypochlorite enhances separation into individual fibers, as illustrated in Report Six, Fig. 18, page 80, the extent to which this phenomenon alone influenced freeness is somewhat obscure. Nevertheless, there is no doubt that alkali extraction does have a significant influence on fiber properties under circumstances where the factor of separation into individual fibers has been minimized or possibly eliminated. This was illustrated in Report Three, Table XII on page 51, Fig. 16 on page 53, and Fig. 17 on page 54.

When the above information is taken into account, apparently both time of alkali extraction and the amount of hypochlorite influence freeness.

From the data in Table I, it also appears there is no clear gain in freeness when using buffered hypochlorite. As a generalization, the relative advantage or disadvantage of buffering the hypochlorite is not clearly demonstrated by these data.

TABLE I

EXPLORATORY HYPOCHLORITE BLEACHING AFTER CHLORINE DIOXIDE-ALKALI DELIGNIFICATION WITH ALKALI CONDITIONING

I. Alkali conditioning

As for II-2 in Report Six, Table V, page 32; yield, 94.6%; Code PP-I.

II. Chlorine dioxide reaction on PP-1

As on LL-1 in Report Six, Table IX, page 45; yield, 89.2%; Code PP-II.

III. Alkali extraction of PP-II

Sodium hydroxide, 6.0%; consistency, 8.0%; temp., 60°C.

Code	Time, min.	Final pH	Yield, %	Rejects, % o.d. pulp
PP-III 10	10	12.1	72.3	9.2
PP-III 30	30	12.0	71.8	6.5
PP-III 60	60	11.8	70.8	5.9
PP-III 120	120	11.7	69.7	4.3

IV. Hypochlorite bleaching screened pulp

Consistency, 12.0%; temp., 40°C.; sulfurous acid wash.

Pulp	Available Cl_2, %	NaOH, %	pH (5 min.)	Final pH	Time, min.	GE	Aged GE	C.F. Rev., 100	1000	Yield, % o.d. pulp	"Yield," %
PP-III 10	1.5	1.0	12.0	11.0	40	69.5	67	610	550	93.6	67.7[a]
	2.5	1.25	12.0	11.3	130	73.0	70	590	520	93.5	67.6
	3.5	1.5	12.1	--	>300	78.0	75	530	460	92.0	66.5
	4.5	1.75	12.1	11.0	>300	79.5	77	475	400	86.1	62.2
	1.5	0	9.6	7.8	40	71.0	68	615	555	--	--
	3.0	0	10.5	8.0	115	76.0	72	600	540	--	--
	4.5	0	10.8	7.4	235	78.0	74	550	480	--	--
PP-III 30	1.5	1.0	11.8	11.0	45	69.0	66	600	540	95.0	68.2
	2.5	1.25	11.9	--	125	74.5	72	570	500	93.0	66.8
	3.5	1.5	12.0	--	>300	77.0	74	530	420	93.0	66.8
	4.5	1.75	12.0	11.0	>300	78.5	76	480	405	90.4	64.9
	1.5	0	10.0	8.2	45	70.0	67	600	540	--	--
	3.0	0	10.5	7.8	150	75.5	72	570	490	--	--
	4.5	0	10.9	7.4	260	78.0	75	470	410	--	--
PP-III 60	1.5	1.0	11.8	11.1	50	68.0	65	575	510	97.4	69.0
	2.5	1.25	11.8	11.0	120	73.0	70	520	455	93.6	66.3
	3.5	1.5	12.0	11.2	>300	77.0	74	515	450	93.6	66.3
	4.5	1.75	12.0	11.2	>300	76.5	73	510	400	92.2	65.3
	1.5	0	10.1	7.9	60	72.0	69	570	505	--	--
	3.0	0	10.5	7.6	160	76.5	73	520	460	--	--
	4.5	0	10.9	7.4	>270	78.0	75	455	380	--	--
PP-III 120	1.5	1.0	11.7	11.1	70	71.5	68	565	500	99.7	69.5
	2.5	1.25	11.8	11.2	>300	76.5	74	515	460	98.8	68.9
	3.5	1.5	12.0	--	>300	78.5	76	500	405	99.0	69.0
	4.5	1.75	12.1	11.2	>300	78.0	76	470	390	97.2	67.7
	1.5	0	10.1	7.8	70	74.0	71	555	495	--	--
	3.0	0	10.5	7.8	185	78.5	76	480	410	--	--
	4.5	0	11.0	7.5	>270	80.5	78	450	360	--	--

[a] 93.6 x 72.3, etc.

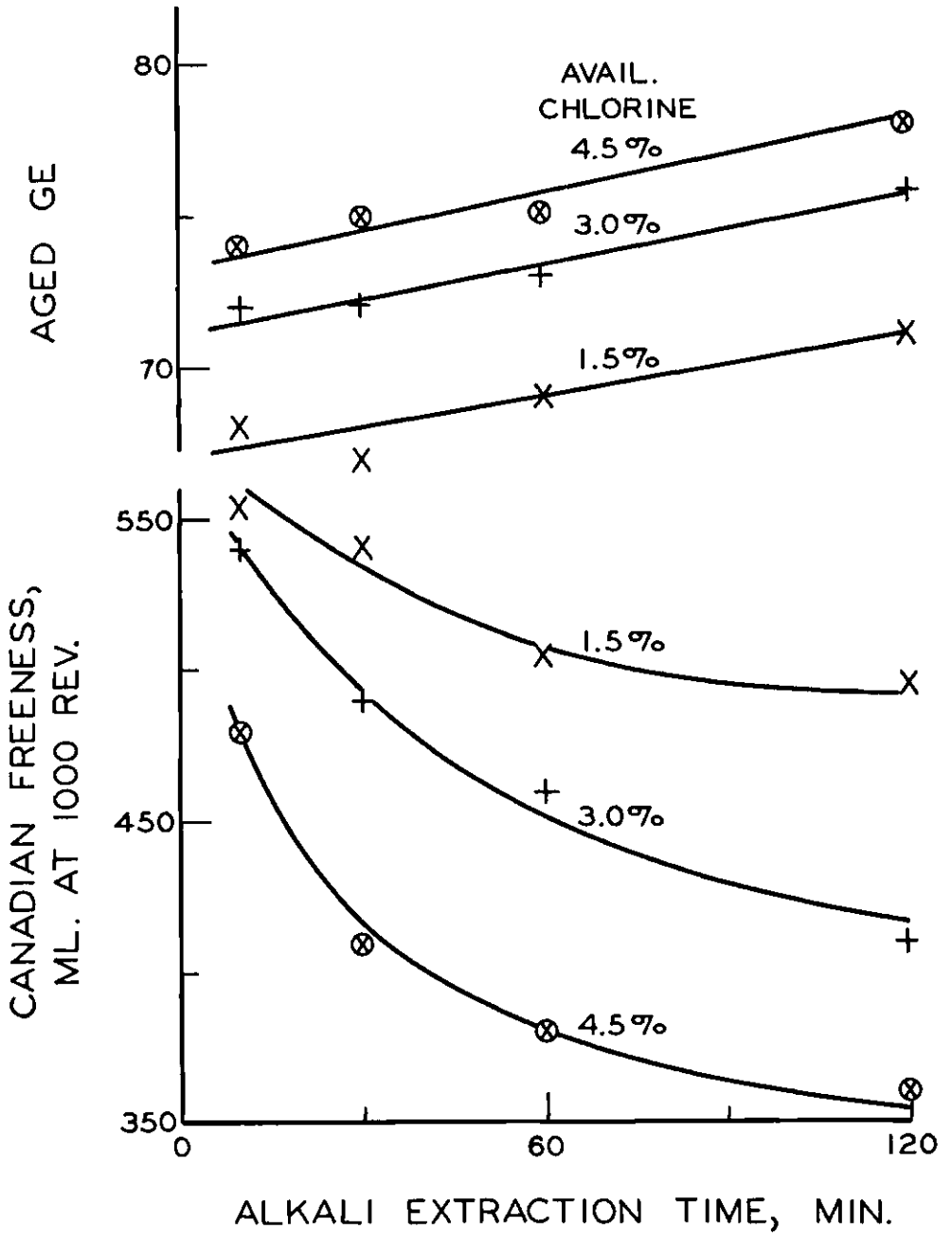

Figure 1. Influence of Alkali Extraction Time with Three Levels of Hypochlorite (15, 30, and 45% Available Chlorine) on Aged GE Brightness and Canadian Freeness for the PP- Pulps

Preparation of Pulps for Handsheets

From consideration of varying alkali extraction and hypochlorite reaction as in Table I, it might be expected that the greatest differences between pulps would be found by a combination of alkali extraction for 10 and 120 min. followed in each case by hypochlorite reaction with 1.5 and 4.5% available chlorine. To determine the extent of the differences between such pulps, they were prepared as shown in Table II. It is noted that while screen rejects were determined only after hypochlorite reaction, there was a marked reduction from the percentage of rejects obtained from the corresponding products in Table I after alkali extraction. This reflects the separation into individual fibers that tends to occur on reaction with hypochlorite as illustrated in Report Six, Fig. 18, page 80, and the fact that fiber liberation was incomplete after alkali extraction.

In addition, it will be noted that after hypochlorite reaction, Pulps PP-2 and PP-4 have yields of near 67 and 63% along with total Klason plus acid-soluble lignin of 2.2 and 1.4% compared with 72 and 68% along with 5.2 and 3.7%, respectively, before hypochlorite reaction.

The four pulps prepared as in Table II, namely, Pulps PP-1, PP-2, PP-3, and PP-4, were used to make handsheets, the primary data for which are given in Table III.

Consideration of Handsheet Data

Handsheet data obtained according to the procedures noted in the experimental part for Pulps PP-1, PP-2, PP-3, and PP-4 may be considered as a group. In each of the following graphs for the PP- pulps, all data for any one pulp are plotted using the symbols shown in Table III.

TABLE II

PREPARATION OF PULPS FOR HANDSHEETS

Alkali Extraction of PP-II

Sodium hydroxide, 6.0%[a]; consistency, 8.0%; temp., 60°C.

Code	Time, min.	Final pH	Yield, %	Klason Lignin, %	Acid-soluble Lignin, %
PP-10 IIIR	10	11.6	71.5	3.3	1.9
PP-120 IIIR	120	11.4	67.6	2.2	1.5

Hypochlorite Reaction with Unscreened Pulps

Sodium hydroxide, 0.25%; consistency, 12.0%; temp., 40°C.; sulfurous acid wash

Pulp	PP-10 III R		PP-120 III R	
Available chlorine, %	1.5	4.5	1.5	4.5
pH after 5 min.	11.3	11.5	11.4	11.5
Final pH	9.8	7.7	9.9	7.9
Time, min.	75	245	110	>270
Yield, %	69.9	67.1	65.8	63.1
Rejects, % o.d. pulp	3.1	0.9	1.3	0.3
Klason lignin, %[b]	--	1.1	--	0.7
Acid-soluble lignin, %[b]	--	1.1	--	0.7
GE (screened pulp)	66.0	75.5	71.0	78.0
Aged GE	64.5	72.5	69.0	75.5
C.F. (100 rev. counts)[c]	570	495	480	450
C.F. (1000 rev. counts)[c]	495	405	430	375
Code	PP-1	PP-2	PP-3	PP-4

[a] All percentages on o.d. fiberized chip basis, with exceptions as noted.

[b] Single determination on screened pulp corrected for yield using total yield data.

[c] British disintegrator.

TABLE III

PRIMARY HANDSHEET DATA FOR PP- SERIES HOLOPULPS[a]

Pulp	PP-1 ◐				PP-2 ●				PP-3 ◒				PP-4 ○			
Canadian freeness, ml.	460	380	290	220	415	360	265	215	385	335	275	220	370	320	250	215
Beating time, min.	2	6	18	24	1	5	12	18	1	3	9	12	0	3	5	7
Density, g./cc.	0.688	0.720	0.754	0.767	0.728	0.741	0.774	0.799	0.738	0.746	0.774	0.791	0.764	0.779	0.799	0.783
Opacity, %	69.0	69.6	65.9	64.6	70.0	68.2	65.1	61.0	68.9	69.8	66.8	64.5	69.6	67.7	66.9	64.3
Breaking length, km.	6.69	7.78	8.85	9.41	7.78	8.49	9.12	9.82	7.48	7.82	9.00	9.62	8.20	8.53	8.95	9.42
Stretch, %	2.3	2.6	2.8	2.8	2.7	2.8	2.8	2.8	2.8	3.0	3.2	3.2	3.0	3.1	3.1	3.0
Tensile energy absorption, g.cm./cm.^{2}	66.4	85.7	107	114	88.0	100	106	115	89.1	98.3	123	130	106	109	115	117
Tensile stiffness, Et , kg./cm.	469	520	554	548	491	510	544	576	475	499	531	526	504	534	534	550
Burst factor	35.8	42.7	50.9	57.0	42.1	50.9	56.6	58.6	42.4	44.6	53.3	57.2	49.4	51.1	53.6	55.5
Tear factor (Elmendorf)	56.4	56.6	51.8	51.2	54.5	51.0	50.6	48.8	56.4	58.3	55.6	56.0	50.2	50.0	50.1	49.7
Tear factor x yield/65	60.6	60.8	55.7	55.0	56.2	52.6	52.2	50.4	57.1	59.0	56.3	56.7	48.7	48.5	48.6	48.2
In-plane tear, g.cm./cm.	41.9	44.7	44.8	42.5	42.8	42.3	41.1	40.0	47.0	47.8	46.3	45.4	41.6	41.9	37.1	42.9
Zero-span breaking length, km.	14.8	17.0	17.1	18.6	16.3	16.4	17.8	17.7	16.7	17.6	17.3	18.0	16.3	16.5	16.2	16.4
Zero-span breaking length x yield/65	15.9	18.3	18.4	20.0	16.8	16.9	18.4	18.3	16.9	17.8	17.5	18.2	15.8	16.0	15.7	15.9
z-direction tensile, kg./cm.^{2}	13.5	18.5	25.3	27.0	20.3	22.6	28.4	34.8	18.5	19.6	27.8	26.0	25.4	28.7	30.3	27.1
M.I.T. fold	91	174	621	807	158	235	554	785	181	242	571	733	236	470	458	536

[a] For test details see Experimental, Pulp Evaluation.

Figure 2 shows beating time versus Canadian freeness. From this it will be observed that the pulps are ranked in such a way that the ascending numerical coding coincides not only with more rapid beating to a given freeness but also with a narrowing freeness range. In other words, Pulps PP-1 and PP-4, which had the maximum and minimum yield, respectively, for the group of four pulps, were not only the slowest and fastest beating pulps but also showed the greatest differences in freeness properties. The more restricted freeness range of the PP- pulps compared with a laboratory kraft pulp, prepared from the same chips as fiberized for the PP- pulps, can be seen by comparing the data in Table IV with the kraft pulp data in Table V which includes beating times to 600, 500, 400, 300, and 200 Canadian freeness. For any one of the PP- pulps, the freeness range began at 500 ml. for only one pulp and began at nearer 400 ml. for the others, so the PP- pulps have lower initial freeness values than the reference kraft pulp.

The relationship of beating time to handsheet density, as in Fig. 3, shows a somewhat analogous situation to Fig. 2. Pulps PP-1 and PP-4 provided the lowest and highest density handsheets for the group of four pulps. Furthermore, the more restricted density range of the PP- pulps is readily apparent by comparing the data in Table VI with the wider 0.59-0.80 range of densities derivable from kraft handsheet data as in Table V. For any one of the PP- pulps, the handsheet density range covered not more than two of the five densities, namely, 0.59, 0.65, 0.69, 0.75, and 0.80, included in Table V.

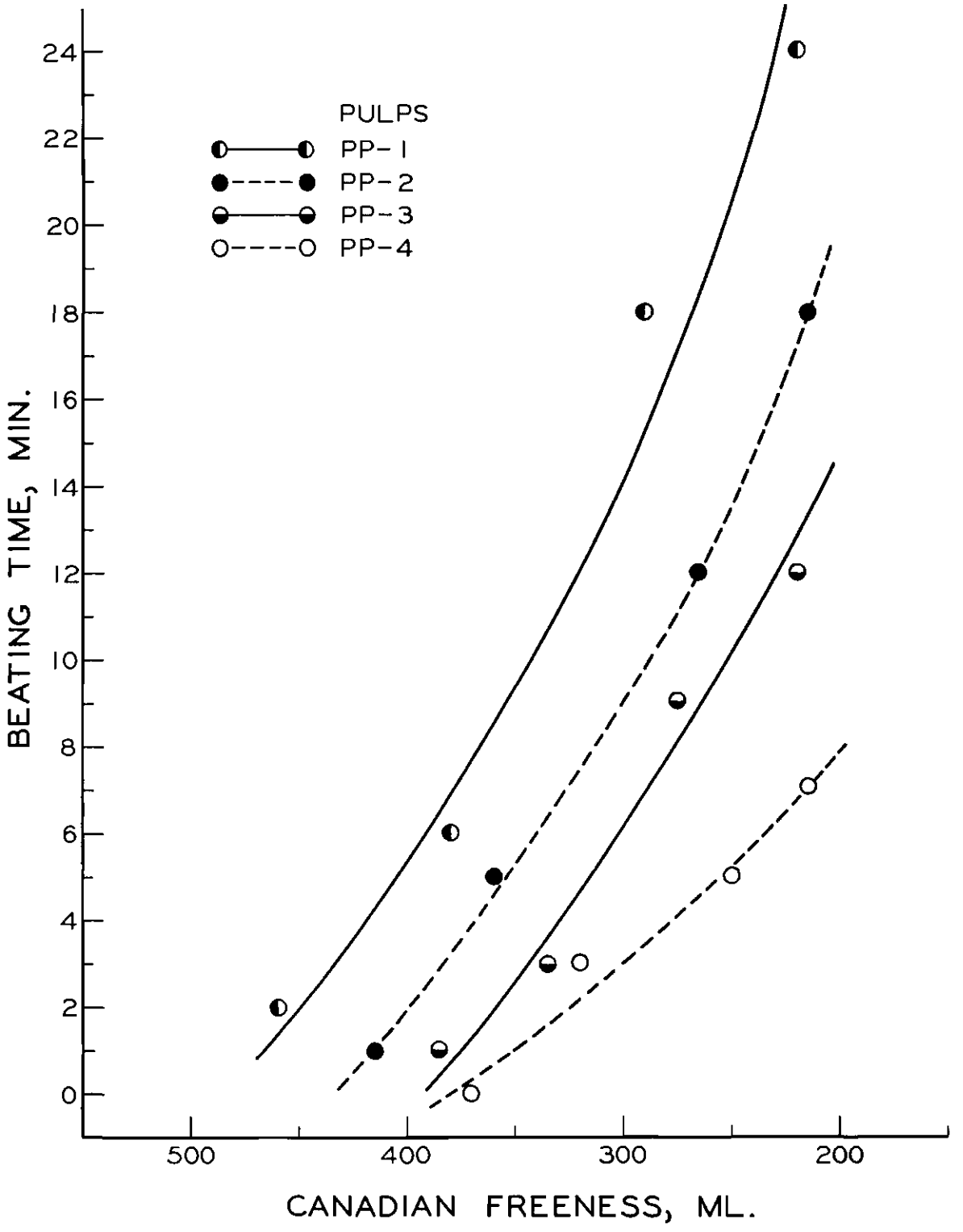

Figure 2. Beating Time in Valley Beater Versus Canadian Freeness for the PP- Pulps

TABLE IV

CANADIAN FREENESS VS. BEATING TIME FOR PP- PULPS[a]

Pulp	Canadian Freeness, ml.	Beating Time, min.
PP-1 ◐	500	0
	400	5
	300	14
	200	30
PP-2 ●	400	2
	300	9
	200	20
PP-3 ◒	400	0
	300	6
	200	15
PP-4 ○	400	0
	300	3
	200	8

[a] For test details, see Experimental, Pulp Evaluation.

TABLE V

HANDSHEET DATA FOR ASPEN KRAFT REFERENCE PULP[a]

	Primary Data					Interpolated Values at Various Handsheet Densities					Interpolated Values at Various Freeness Levels				
Canadian freeness, ml.	600	530	470	340	185	620	530	470	370	280	600	500	400	300	200
Beating time, min.	0	5	10	20	35	0	5	10	17	25	0	8	15	24	33
Density, g./cc.	0.596	0.656	0.695	0.776	0.845	0.59	0.65	0.69	0.75	0.80	0.60	0.67	0.73	0.79	0.84
Opacity, %	95.4	94.2	92.2	88.8	82.0	--	--	--	--	--	--	--	--	--	--
Breaking length, km.	5.55	7.23	8.33	9.99	10.6	5.4	7.1	8.2	9.5	10.4	5.6	7.8	9.3	10.2	10.6
Stretch, %	1.2	1.7	2.0	2.9	3.0	1.1	1.6	2.0	2.5	2.9	1.2	1.9	2.5	2.9	3.0
Tensile energy absorption, g.cm./cm.^{2}	27.9	49.7	66.5	118	133	26	50	66	90	112	28	58	86	112	134
Tensile stiffness, Et , kg./cm.	584	613	638	638	670	580	610	625	645	660	585	620	640	660	670
Burst factor	21.0	31.3	41.4	56.7	65.3	20	30	40	52	60	21	36	50	59	65
Tear factor (Elmendorf)	57.6	70.1	73.8	73.1	59.4	57	69	74	74	69	58	72	75	71	61
Tear factor x yield/65	44.7	54.5	57.3	56.8	46.1	44	54	57	58	54	45	56	58	55	47
Zero-span breaking length, km.	20.0	20.9	20.6	20.0	19.7	20	21	21	20	20	20	21	20	20	20
Zero-span breaking length x yield/65	15.5	16.2	16.0	15.5	15.3	16	16	16	16	16	16	16	16	16	15
M.I.T. fold[b]	3	11	47	434	1717	3	10	50	290	825	3	25	185	670	1500

[a] June, 1967. Standard 5.5-kg. weight on the end of the bedplate lever.

[b] Data were obtained on 15-month-old handsheets.

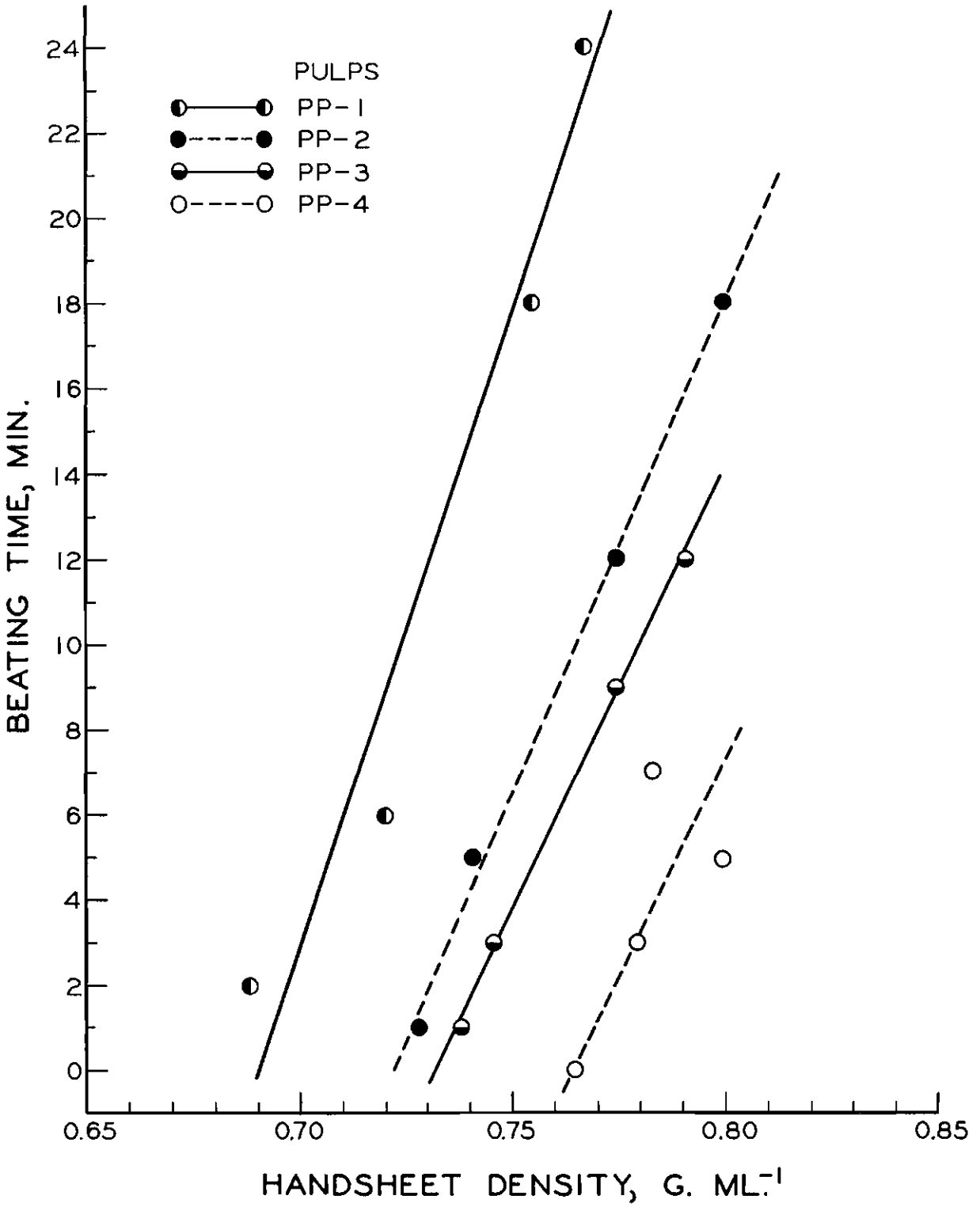

Figure 3. Beating Time in Valley Beater Versus Handsheet Density for the PP- Pulps

TABLE VI

HANDSHEET DENSITY VS. BEATING TIME FOR PP- Pulps

Pulp		Handsheet Density, g./cc.	Beating Time, min.
PP-1	◐	0.69	0
		0.75	18
PP-2	●	0.75	6.5
		0.80	18
PP-3	◒	0.75	4
		0.80	14
PP-4	○	0.75	--
		0.80	7.5

To further consider the PP- pulps, in Fig. 4-12 handsheet density is plotted versus the following:

Fig. 4: opacity, %,

Fig. 5: burst factor, and z-tensile, kg.-cm.$^{-2}$,

Fig. 6: breaking length, km.,

Fig. 7: tensile energy absorption, g. cm. cm.$^{-2}$,

Fig. 8: stretch, %, and tensile stiffness, kg. cm.$^{-1}$,

Fig. 9: Elmendorf tear factor and in-plane tear, g. cm. cm.$^{-1}$,

Fig. 10: Elmendorf tear factor x yield/65,

Fig. 11: zero-span breaking length x yield/65, km., and zero-span breaking length, km.,

Fig. 12: M.I.T. fold.

As applied for the PP- pulps in Fig. 2 and 3, similar rankings occur in Fig. 4, 5, and 6 regarding opacity, burst factor, and breaking length.

In Fig. 7, 8, and 9, tensile energy absorption, tensile stiffness, stretch, and in-plane tear data on chlorine dioxide-alkali pulps are presented for

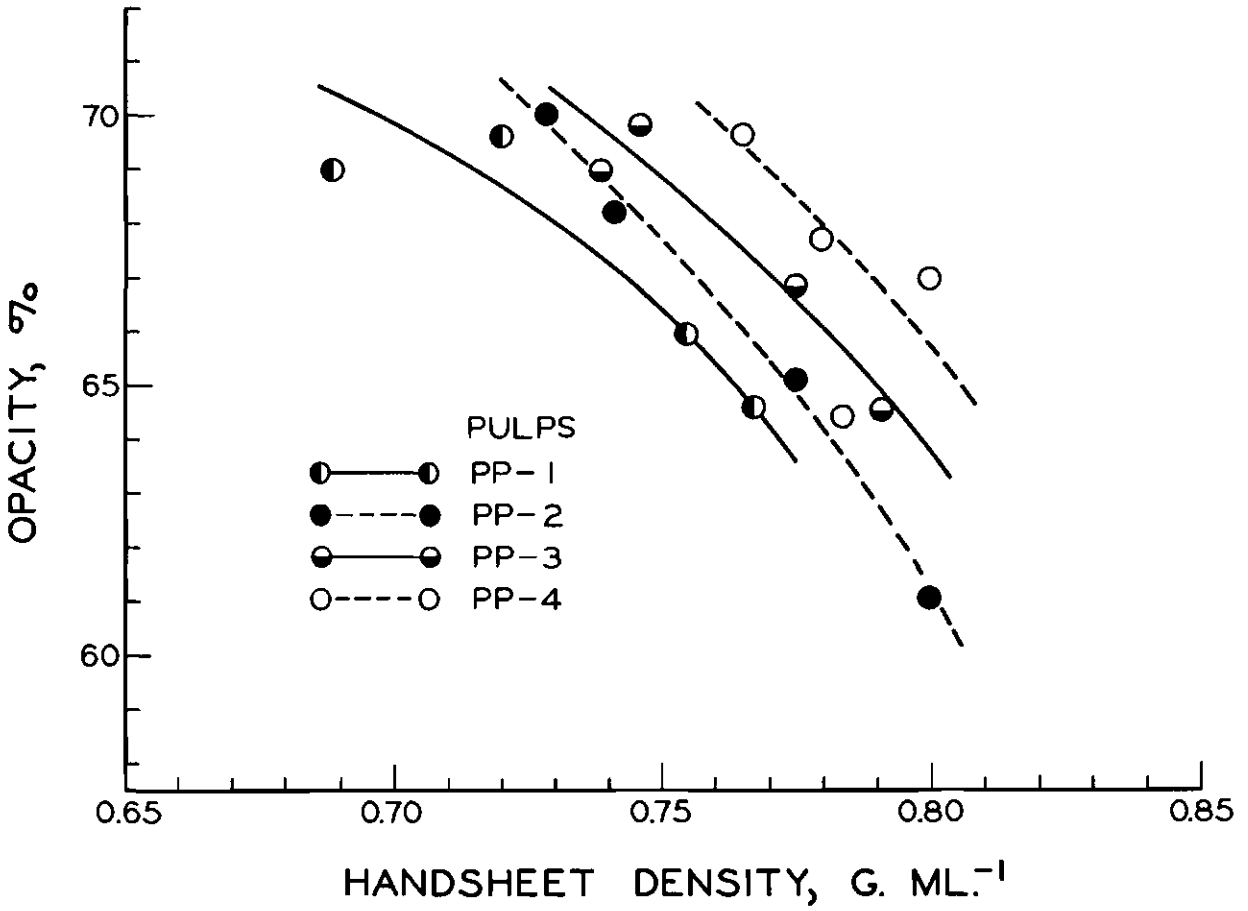

Figure 4. Relationship Between Opacity of 60 g.s.m. Handsheets and Handsheet Density for the PP- Pulps

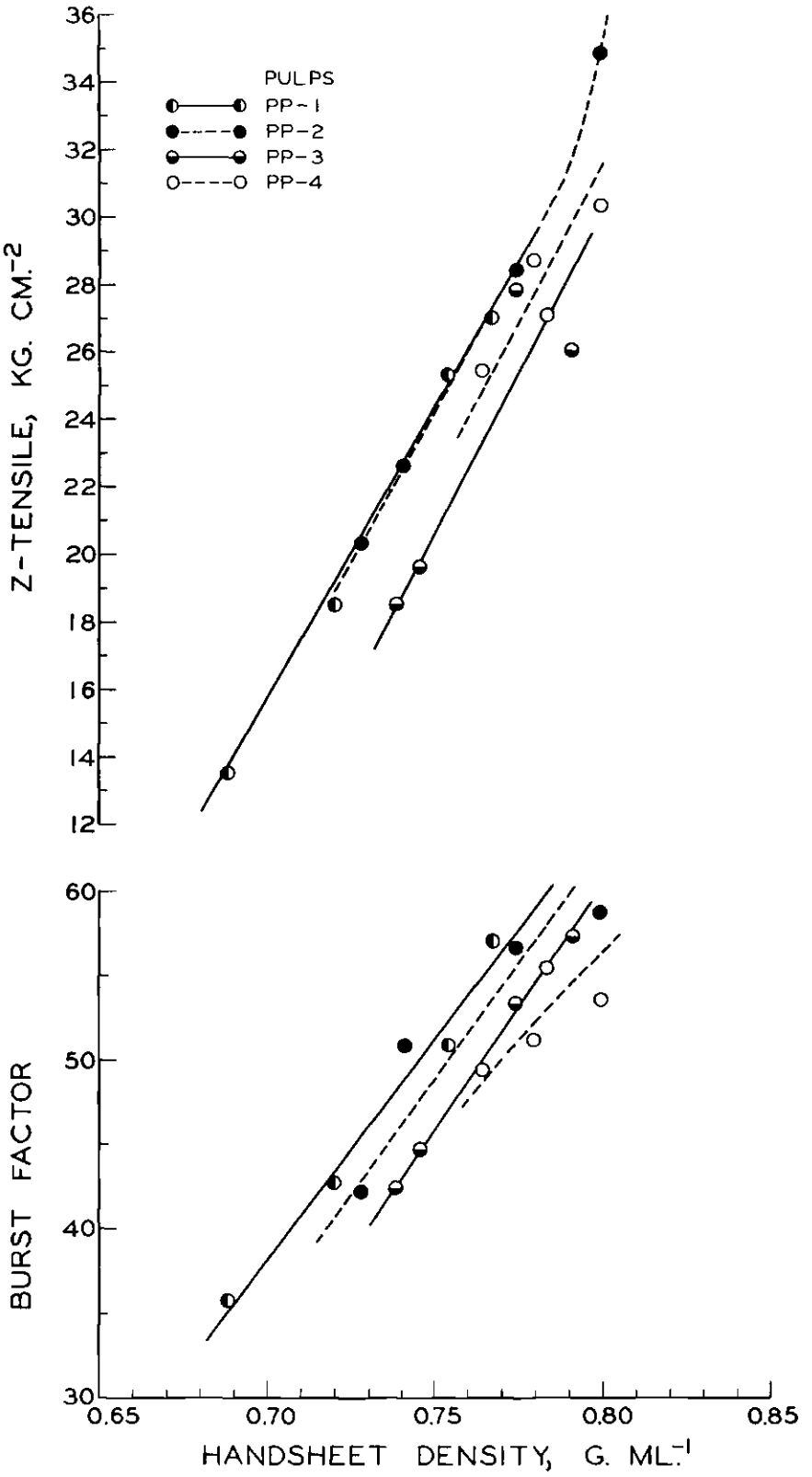

Figure 5. Effect of Handsheet Density on z-Tensile Strength and Burst Factor for the PP- Pulps

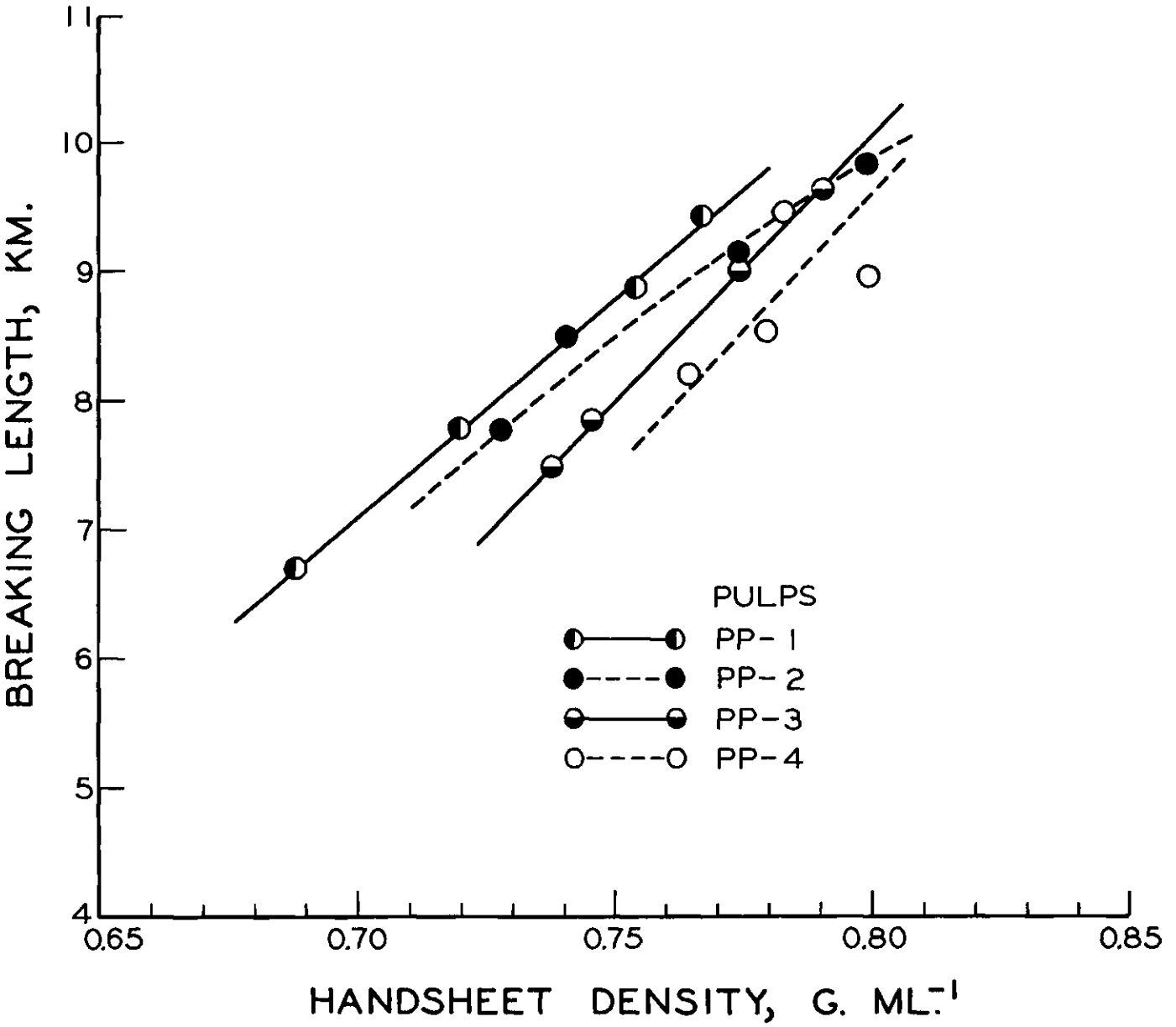

Figure 6. Relationship Between Breaking Length and Handsheet Density for the PP- Pulps

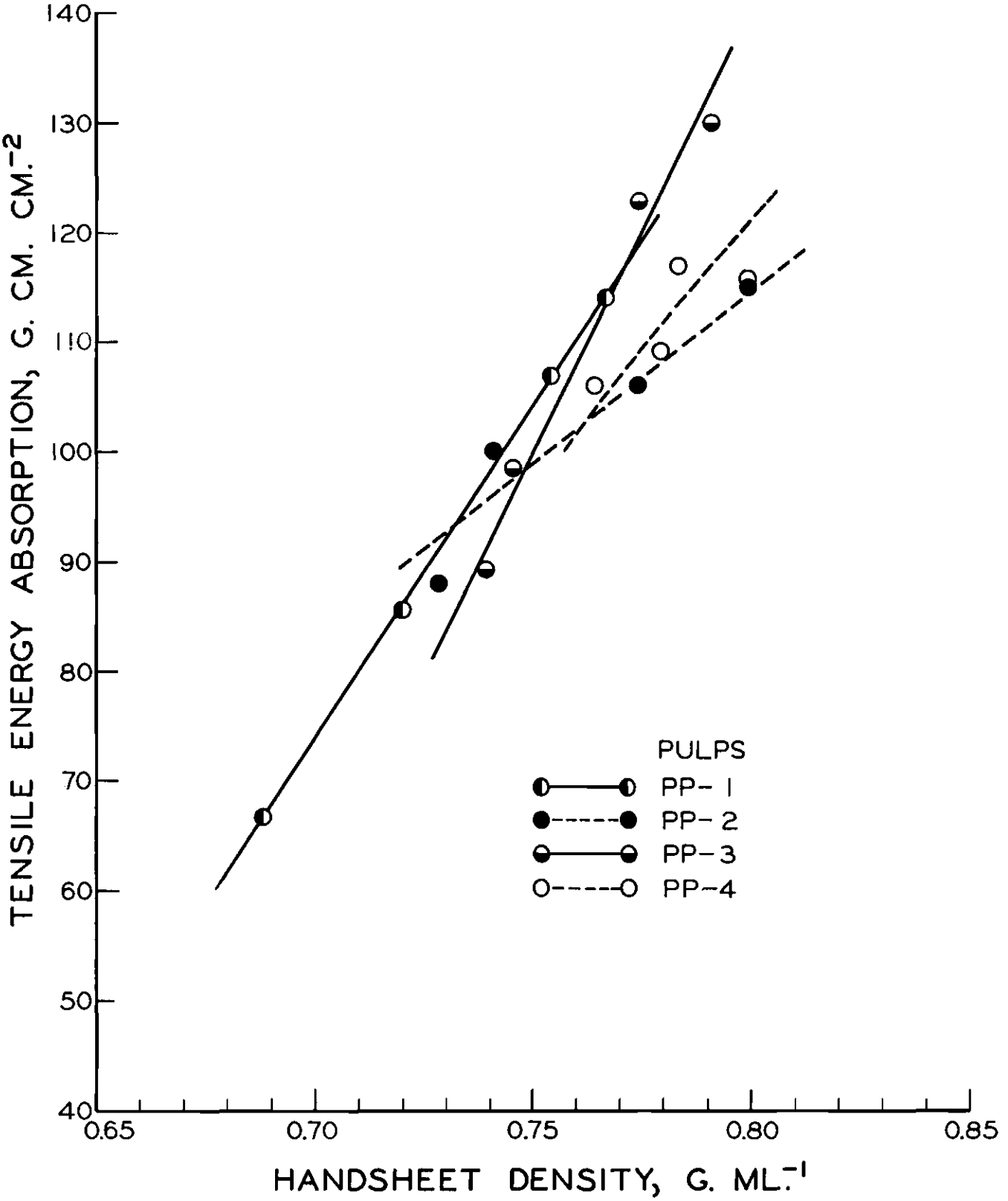

Figure 7. Relationship Between Tensile Energy Absorption and Handsheet Density for the PP- Pulps

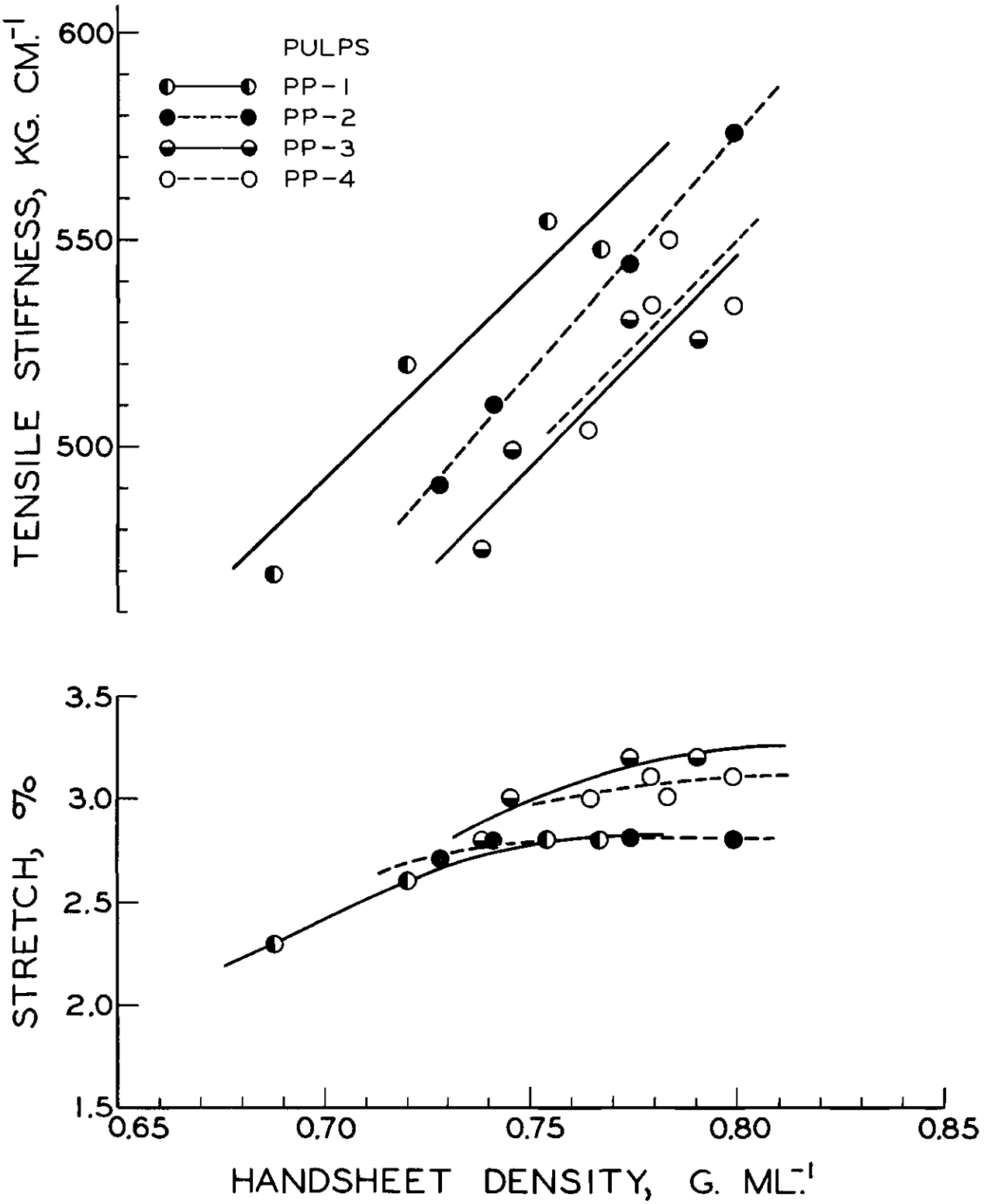

Figure 8. Effect of Handsheet Density on Tensile Stiffness and Stretch for the PP- Pulps

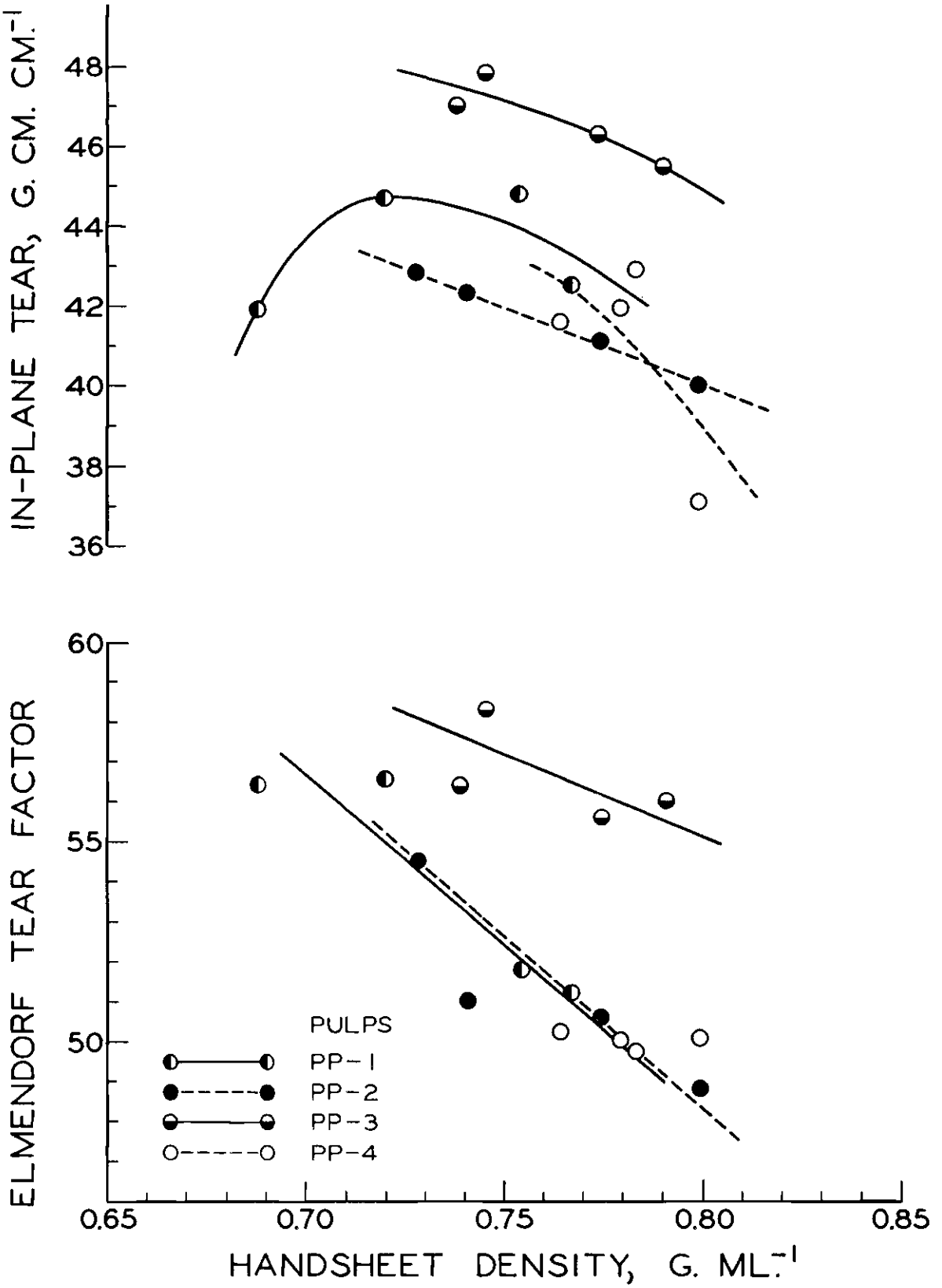

Figure 9. Effect of Handsheet Density on In-Plane Tear and Elmendorf Tear Factor for the PP- Pulps

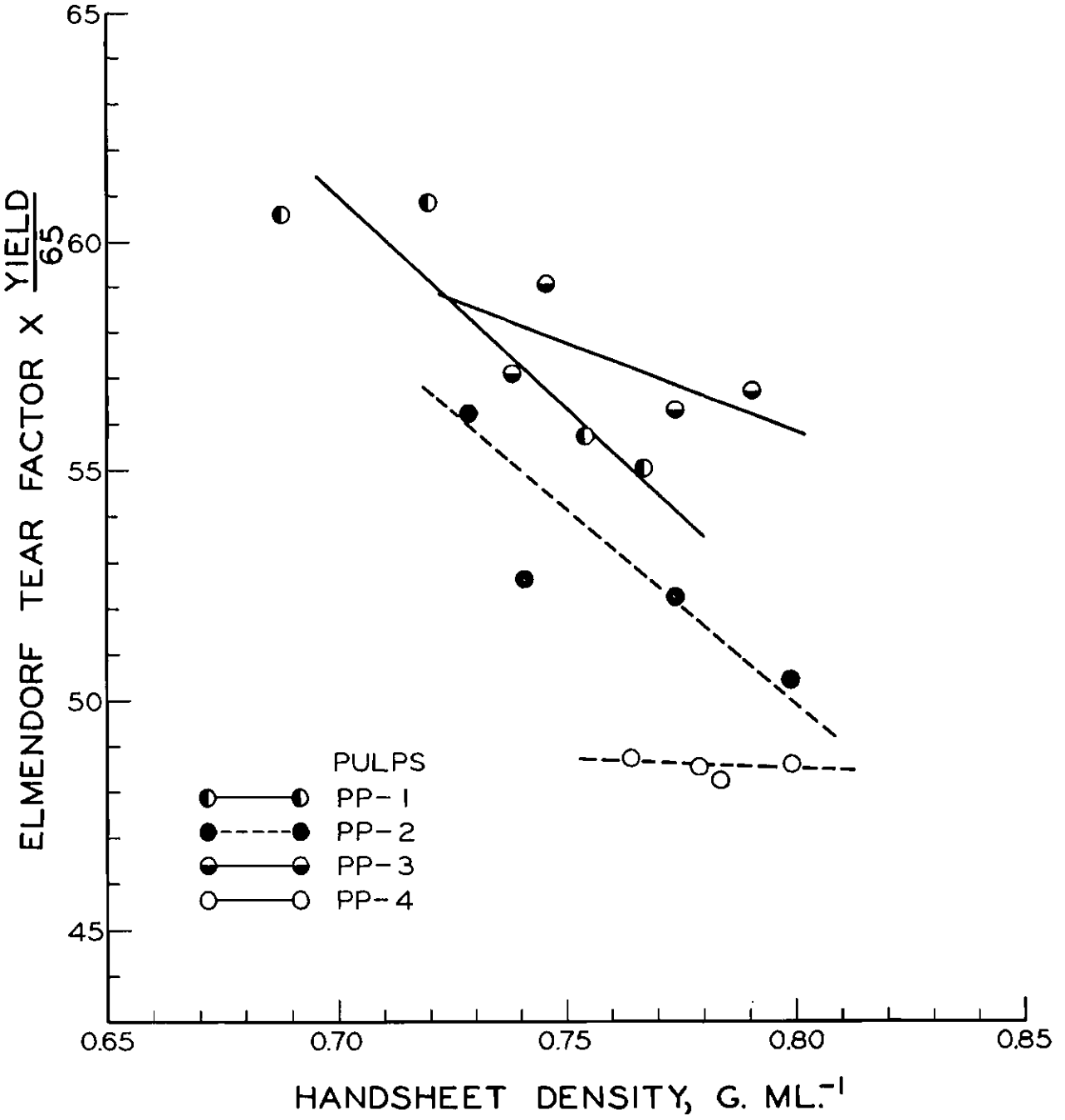

Figure 10. Relationship Between Elmendorf Tear Factor x Yield/65 and Handsheet Density for the PP- Pulps

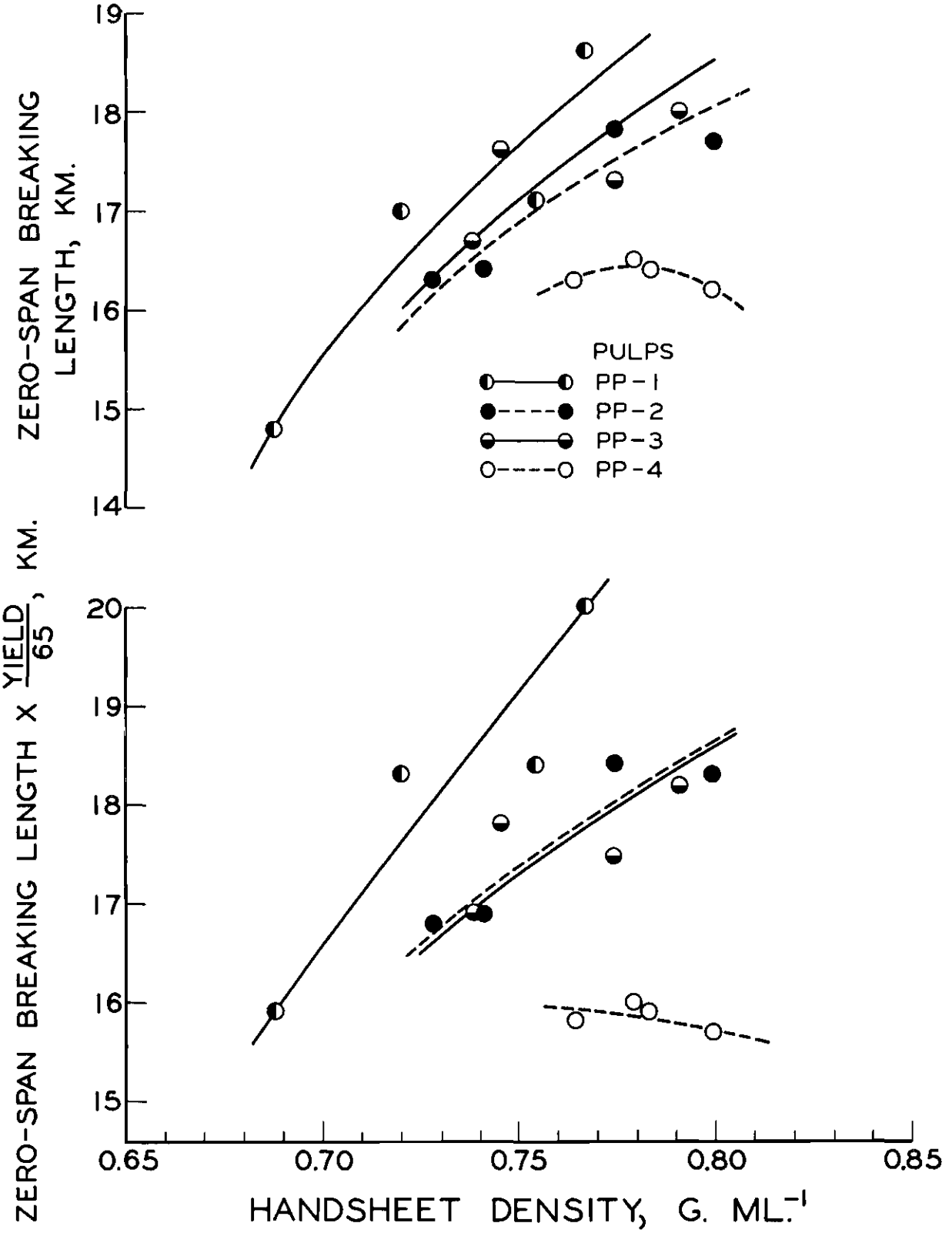

Figure 11. Effect of Handsheet Density on Zero-Span Breaking Length and Zero-Span Breaking Length x Yield/65 for the PP- Pulps

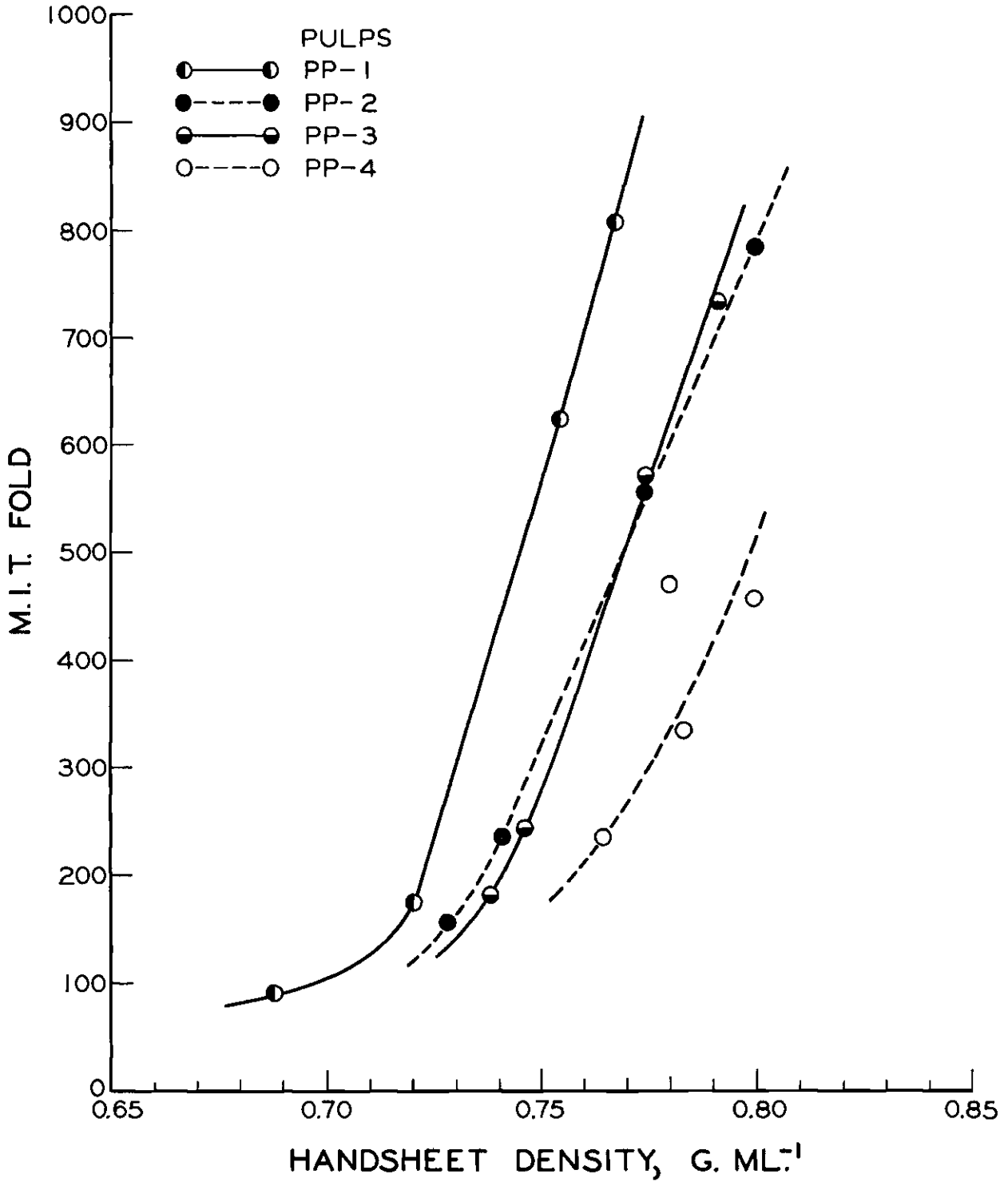

Figure 12. Relationship Between M.I.T. Fold and Handsheet Density for the PP- Pulps

the first time. Elmendorf tear factor and zero-span breaking length data for Pulps PP-1, PP-2, PP-3, and PP-4 are included to provide a more complete picture. Later in this report, reference will be made both to how these handsheet properties may be compared with those of the kraft reference pulp and to some information available on a commercial bleached kraft pulp.

At this point, a positive conclusion is that the PP- pulps may be regarded as providing handsheets with freeness values and densities that encompass only the lower freeness and higher density ranges covered by handsheets provided from the kraft reference pulp. In addition, changes in process conditions were associated with notable differences in fiber properties. If Pulps PP-1 and PP-2 are compared with Pulps PP-3 and PP-4, the former appear to be more desirable on the basis of beating properties and handsheet data. Since the principal difference in producing these two pairs of pulps lay in the time of alkali extraction, which was 10 min. for Pulps PP-1 and PP-2 compared with 120 min. for Pulps PP-3 and PP-4, it seems likely that the length of time the fibers are exposed to alkali is associated with changes in fiber properties. This is consistent with the findings in Report Six, Table XV, page 61 et seq., where it was indicated that with increased time of alkali extraction, changes in the saccharide units of the polysaccharides occur without a parallel degree of detachment of the changed groups. At present, more precise information concerning the nature of these changes is not available.

However, it is known from consideration of the role of alkali extraction as discussed in Report Six, pages 44-70, that at an extraction temperature of 60°C. a substantial part of the total modified lignin removal by alkali would have occurred in 10 min. In 120 min., about 2% more would be removed, and from the lignin analyses in Table II above it is confirmed that if the main function of alkali extraction is to be removal of modified lignin, there is no marked gain in delignification achieved by extending the time. Under circumstances where the

alkali extraction is of quite short duration, it is also known from the results described in Report Six, for example, Table XII, page 50, that screen rejects will be high, or in other words, fiber liberation will be incomplete.

Thus, it is recognized that alkali extraction at 60°C., for example, can function to rapidly remove modified lignin, and through extension of time, extraction can also function to provide liberation of fibers with a decrease in screen rejects to an acceptable level. In addition, increased time of alkali extraction is not only associated with changes in the polysaccharides but also contrarily associated with an apparently undesirable shift in fiber properties as revealed by beating and handsheet data. Therefore, it is pertinent to consider the case where the choice of process conditions in chlorine dioxide-alkali pulping acknowledges this situation.

CHLORINE DIOXIDE-ALKALI PULPING WITHOUT ALKALI CONDITIONING

DISCUSSION

Introductory Comment

If alkali extraction time has a significant influence on beating and handsheet data when a chlorine dioxide-alkali pulp is made, then it is desirable to reconsider the information in Report Six, Table V, page 32. In that table under Columns II-1 and II-2 are shown data for fiberized chips that had undergone oxidative reaction with 9.0% chlorine with and without alkali conditioning. Although the total modified lignin content was nearly the same for both products after oxidative reaction, with subsequent alkaline extraction fewer screen rejects were obtained when alkali conditioning was included. Hence, further work was pursued following the pathway indicated by Column II-2.

What happens when alkali conditioning is omitted will now be considered.

Varying Alkali Extraction After Oxidative Reaction

Using fiberized chips from the same lot made for preparing the PP- pulps, exploratory alkali extractions after oxidative reaction were carried out to provide data as in Table VII. From this it will be seen that, at 60°C., extraction for 10 and 120 min. with 6.0 or 9.0% sodium hydroxide would be expected to provide products with certain relationships to the two extracted products in Table II. For 9.0% sodium hydroxide the reaction times and final pH data would be expected to be almost identical; yield, screen rejects, and Klason plus acid-soluble lignin contents would be expected at least to overlap as seen from Table VIII. For the use of 6.0% sodium hydroxide, while the extraction times and amount of alkali would be the same as for the extraction of the PP- pulps, with alkali conditioning omitted, the expected final pH values would be lower, which would mean the alkali extractions

TABLE VII

DELIGNIFICATION WITHOUT ALKALI CONDITIONING

Chlorine dioxide reaction:

Chlorine dioxide, %	9.0	Sodium hydroxide, %	3.5
Initial temp., °C.	25	Consistency, %	6.0
Temp. after 60 min., °C.	35	pH after 5 min.	6.7
Time, min.	295	Final pH	2.6
Yield, %	94.9	Code	00-I

Exploratory alkali extraction of 00-I at 8.0% consistency and 60°C.:

	Sodium Hydroxide, %	Time, min. 10	60	240
pH after 5 min.	6.0	11.7	11.7	11.7
	7.5	12.0	12.0	12.0
	9.0	12.1	12.1	12.1
Final pH	6.0	10.7	9.5	8.7
	7.5	11.6	10.8	10.7
	9.0	11.9	11.6	11.6
Yield (Y), %	6.0	82.2	79.8	78.2
	7.5	77.7	75.5	71.7
	9.0	76.9	70.8	70.6
Screen rejects, % o.d. pulp	6.0	15.4	13.8	10.9
	7.5	9.9	8.0	6.5
	9.0	7.4	6.4	5.5
Analysis:				
Acetone-soluble lignin, %	6.0	3.1	3.9	2.4
Klason lignin, %	6.0	5.9	4.7	4.6
Acid-soluble lignin, %	6.0	2.7	1.8	2.1
Total modified lignin, %	6.0	11.7	10.4	9.1
Acetone-soluble lignin, %	7.5	2.9	3.2	3.1
Klason lignin, %	7.5	4.8	4.1	3.9
Acid-soluble lignin, %	7.5	2.0	1.4	1.4
Total modified lignin, %	7.5	9.7	8.8	8.4
Acetone-soluble lignin, %	9.0	3.4	2.5	1.0
Klason lignin, %	9.0	4.3	3.6	3.6
Acid-soluble lignin, %	9.0	1.7	1.3	1.6
Total modified lignin, %	9.0	9.4	7.4	6.2
Yield minus modified lignin, %	6.0	70.5	69.4	69.1
	7.5	68.0	66.7	63.3
	9.0	67.5	63.4	64.4

TABLE VIII

SELECTED DATA FROM TABLES I, II, AND VII

Alkali Extraction: Consistency, 8.0%; Temp., 60°C.

Material extracted	PP-II	PP-II	OO-I	OO-I	OO-I	OO-I
Sodium hydroxide, %	6.0	6.0	9.0	9.0	6.0	6.0
Time, min.	10	120	10	120	10	120
Final pH	12.1, 11.6	11.7, 11.4	11.9	11.6[a]	10.7	9.1[a]
Yield, %	72.3, 71.5	69.7, 67.6	76.9	70.7[a]	82.2	79.0[a]
Screen rejects, %	9.2	4.3	7.4	6.0[a]	15.4	12.5[a]
Klason + acid-sol. lignin, %	5.2	3.7	-	-	-	-
Total modified lignin, %	-	-	9.4	7.0[a]	11.7	9.8[a]

[a] Estimated from Table VII.

would be milder. Under these circumstances, higher yields, higher screen rejects, and higher Klason plus acid-soluble lignin comtents would be expected on the basis of the data collected in Table VIII. However, it will be noted from Table VII that under the milder alkaline conditions about the same amount of acetone-soluble modified lignin was unremoved as when 9.0% sodium hydroxide was used for short extraction times. Thus, extraction for 10 min. with 6.0% sodium hydroxide would permit consideration of a situation where modified lignin removal would be carried out more independently of other possible changes associated with alkali extraction.

Exploratory Experiments After Chlorine Dioxide-Alkali Delignification

Chlorine dioxide-reacted fiberized chips were extracted for 10 and 120 min. with 6.0 and 9.0% sodium hydroxide to give four products in yields of 81.5, 77.1, 72.3, and 67.7%, respectively, as indicated in Table IX. Final pH data were in line with expectations, and although yield data were not as expected from Table VIII, yields were acceptable for comparisons with PP- pulps.

As was found when reacting chlorine dioxide-alkali pulps prepared with alkali conditioning (Report Six, Table XX, page 76), neither chlorine dioxide nor alkaline peroxide provided a satisfactory brightness gain. Hypochlorite gave more satisfactory results.

Preparation of Pulps for Handsheets

For simplification, pulps for handsheets were prepared by reaction of the four unscreened alkali extraction products with hypochlorite using 4.5% available chlorine only and omitting reaction with 1.5% as included when making the PP- pulps. Data related to hypochlorite reactions are given in Table X. The screened pulps have been identified on a descending total yield basis as Pulps 00-1, 00-3, 00-2, and 00-4.

TABLE IX

EXPLORATORY BLEACHING AFTER CHLORINE DIOXIDE-ALKALI DELIGNIFICATION

Chlorine Dioxide Reaction

00-I, 94.9%[a] yield; Table VII

Alkali Extraction of 00-I (8.0% consistency; temp., 60°C.)

Pulp code	00-I-1	00-I-3	00-I-2	00-I-4
Sodium hydroxide, %	6.0	6.0	9.0	9.0
Time, min.	10	120	10	120
Final pH	10.9	9.3	11.9	11.7
Yield, %	81.5	77.1	72.3	67.7
Klason + acid-sol. lignin, %[b]	7.8 + 3.5	7.0 + 3.2	5.2 + 2.3	3.8 + 1.7

Bleaching (12.0% consistency)

	00-I-1		00-I-3		00-I-2		00-I-4	
Chlorine dioxide, %	0.5	1.5	0.5	1.5	0.5	1.5	0.5	1.5
Temp., °C. (start/2 hr.)	40/60							
Final pH	4.5	3.2	4.4	3.0	4.3	2.9	4.2	2.6
Time, min. (starch/I^-)	40	125	40	170	55	180	75	260
GE (after 600 rev. counts)	--	--	57.5	63.2	--	--	62.3	67.0
Heat-aged GE	--	--	51.0	54.8	--	--	56.8	59.7
Yield, %	77.6	76.3	74.3	72.3	71.3	69.8	63.8	63.1
Peroxide[c], % (210 min./60°C.)	0.5	1.5	0.5	1.5	0.5	1.5	0.5	1.5
Final pH	7.6	8.0	7.6	8.0	7.8	8.2	8.2	8.5
Residual peroxide, %	0.13	0.74	0.21	0.73	0.21	0.88	0.24	0.89
GE (after 600 rev. counts)	--	58.8	--	58.5	--	63.2	59.1	66.6
Yield, %	79.9	76.5	72.9	70.9	69.0	67.3	62.1	62.7
Hypochlorite, % available Cl_2 (40°C.)	1.5	4.5	1.5	4.5	1.5	4.5	1.5	4.5
pH after 5 min. (0.25% NaOH)	10.7	11.4	11.1	11.5	11.2	11.3	11.4	11.6
Final pH	9.7	8.3	9.9	8.6	10.2	8.2	10.2	8.2
Time, min. (starch/I^-)	25	180	30	190	25	180	60	240
GE (after 600 rev. counts)	--	71.3	--	72.8	--	70.1	78.2	82.6
Heat-aged GE	--	65.4	--	66.9	--	65.4	72.0	77.1
Yield, %	76.8	76.0	72.9	71.1	69.4	67.2	63.8	61.7 (?)

[a] All percentage data on o.d. fiberized chip basis.

[b] Means of duplicate analyses.

[c] Plus 2.5% 40-42°Bé. sodium silicate. The peroxide solution included 0.5 g. Epsom salts/liter, ca. 9-12 g. H_2O_2/liter, and 0.125 g. NaOH/g. H_2O_2.

TABLE X

PREPARATION OF PULPS FOR HANDSHEETS

Chlorine Dioxide Reaction

00-I: 94.9%[a] yield as in Table VII

Alkali Extraction of 00-I

Yield, %: 00-I-1, 81.5; 00-I-3, 77.1; 00-I-2, 72.3; 00-I-4, 67.7 (see Table IX)

Hypochlorite Reaction with Unscreened Pulps

Consistency, 12.0% Temp., 40°C.
Available chlorine, 4.5% Sodium hydroxide, 0.25%

Pulp	00-I-1	00-I-3	00-I-2	00-I-4
pH after 5 min.	11.0	11.1	11.3	11.4
Final pH	8.2	8.2	7.9	7.9
Time, min. (starch/I^-)	150	170	180	235
Total yield, %	76.8	71.6	68.2	66.2
Rejects, % o.d. pulp	17.6	16.9	9.0	4.4
Klason lignin, %[b]	5.0	4.1	2.7	1.9
Acid-soluble lignin, %[b]	3.1	2.7	1.8	1.1
GE (screened pulp)	69.0	70.3	74.1	77.3
Aged GE	63.5	64.8	68.3	72.0
C.F.[c]	690	640	580	460
Code	00-1	00-3	00-2	00-4

[a] All percentages on an o.d. fiberized chip basis with exceptions as noted.

[b] Single determination on screened pulp corrected for yield using total yield data.

[c] After circulation for 5 min. in Valley beater with no bedplate load and 600 rev. counts in British disintegrator at 0.3% consistency.

These pulps, as can be seen from Table X, are associated with screen rejects of from 17.6 to 4.4%. Such high values are at first surprising, especially when in Report Six, page 49, it was concluded that in chlorine dioxide-alkali pulping there is a fiber liberation point at a 71-72% total yield, and in Table X at 71.6% total yield screen rejects are 16.9%, for example. However, since there is no reason to discard the earlier conclusion concerning a fiber liberation point at 71-72% total yield, some consideration of what is responsible for excessive screen rejects as recorded in Table X is appropriate.

In conventional chemical pulping when yields are at or below the fiber liberation point, excessive screen rejects are an indication of cooking nonuniformity. When this does not occur within a digester, excessive screen rejects indicate nonuniformity of cooking within a chip. Although fiberized chips are relatively small, Bauer-McNett classifications as in Report Six, Table XI, page 48, reveal an appreciable range in the size of the fibrous particles. This is also illustrated by Fig. 13. Without any alkali conditioning before oxidative reaction, it appears that for the fiberized chips used there is nonuniform reaction within at least a significant portion of the fiberized chips. Thus, while the time to consume 9.0% chlorine dioxide is not greatly influenced by alkali conditioning, this step has some relevance to uniformity of reaction across fiber bundles. This is in accord with Report Six, Fig. 2 and 3, on pages 21 and 22.

To pursue the question of what happens to fiber properties when alkali conditioning is omitted, the matter of nonuniformity of reaction was put to one side for the time being.

Pulps 00-1, 00-3, 00-2, and 00-4 were used to make handsheets, the primary data for which are given in Table XI.

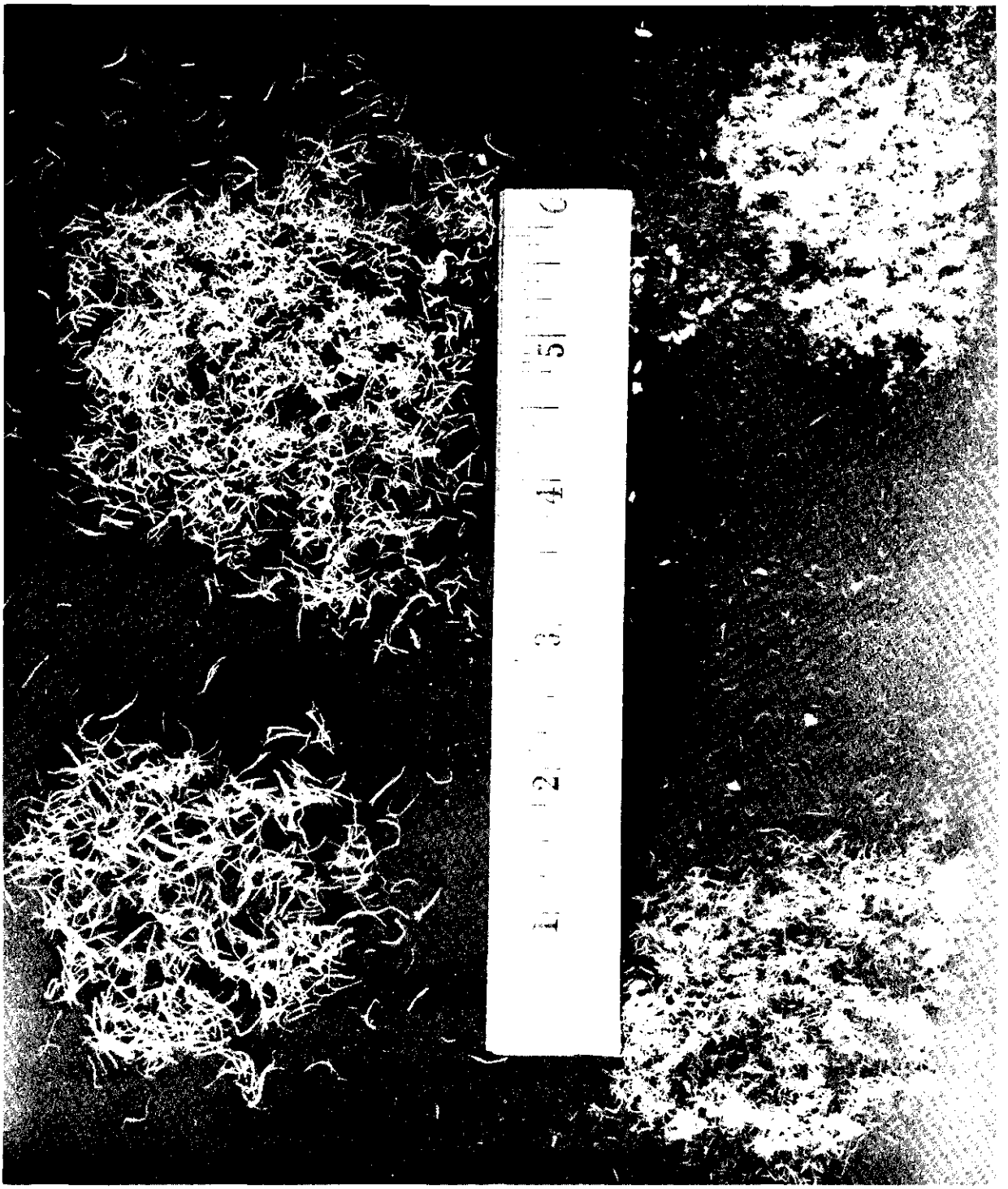

Figure 13. Range in Size of Aspen Fibrous Particles for On-65, -35, -6, and -12-Mesh Bauer-McNett Screens, Considered in Clockwise Order, Starting at the Top Right

TABLE XI

PRIMARY HANDSHEET DATA FOR 00- SERIES PULPS[a]

Pulp	00-1 ◧				00-3 ◨				00-2 ■				00-4 □			
Canadian freeness, ml.	545	380	245	200	500	375	270	210	525	350	275	190	400	350	275	190
Beating time, min.	10	30	38	41	8	15	24	28	1	10	14	18	0	2	5	7
Density, g./cc.	0.541	0.611	0.661	0.681	0.585	0.621	0.672	0.683	0.608	0.696	0.731	0.778	0.687	0.716	0.749	0.784
Opacity, %	75.4	74.4	72.5	70.4	74.2	71.7	69.8	69.0	70.0	68.4	65.2	60.9	67.7	67.7	65.7	61.1
Breaking length, km.	5.92	7.95	9.09	9.38	6.85	7.89	9.19	9.46	6.71	9.25	9.63	10.70	8.59	9.41	10.00	10.80
Stretch, %	1.6	1.9	2.2	2.1	2.0	2.2	2.3	2.3	2.1	2.4	2.4	2.7	2.6	2.7	2.6	2.7
Tensile energy absorption, g.cm./cm.^{2}	37.3	61.5	79.4	78.8	60.0	69.6	86.4	87.0	57.6	91.6	93.7	118	93.1	103	107	117
Tensile stiffness, Et , kg./cm.	436	522	531	567	467	499	537	567	467	558	608	611	526	551	587	615
Burst factor	25.0	39.2	45.2	48.1	35.1	41.2	49.8	52.1	34.6	52.8	59.2	73.7	48.2	54.3	59.7	66.8
Tear factor (Elmendorf)	51.0	48.1	42.4	45.5	53.2	53.2	47.6	46.7	58.3	52.0	50.9	47.4	57.5	53.9	52.8	52.7
Tear factor x yield/65	60.3	56.8	50.1	53.8	58.6	58.6	52.4	51.4	61.2	54.6	53.4	49.7	58.6	54.9	53.8	53.7
In-plane tear, g.cm./cm.	36.9	38.5	37.6	36.5	40.1	42.1	39.1	39.3	45.7	43.6	42.1	42.5	47.9	47.3	46.7	44.3
Zero-span breaking length, km.	14.6	16.4	17.4	17.6	15.7	16.9	17.3	18.1	14.8	17.9	19.2	18.0	16.3	17.4	19.2	19.5
Zero-span breaking length x yield/65	17.3	19.4	20.6	20.8	17.3	18.6	19.1	19.9	15.5	18.8	20.1	18.9	16.6	17.7	19.6	19.9
z-direction tensile, kg./cm.^{2}	7.25	12.0	15.4	18.3	9.2	11.7	17.5	18.3	10.5	17.7	23.2	29.1	18.6	19.8	23.7	29.3
M.I.T. fold	26	89	227	340	55	104	288	421	74	336	557	1027	256	380	696	1205

[a] For test details see Experimental, Pulp Evaluation.

In a number of previously prepared pulps, including some of those as in Table I, Report Six, an undesirable tendency for wet handsheets to stick to the handsheet machine wire was observed. This kind of observation has been made previously, for example, by Watson and Phillips (1) who noted pulps obtained using chlorite and alkali led to wet handsheets that tended to stick to the wire and often ruptured when being removed. No similar tendency for wet handsheets to stick to the wire was observed in the OO- and PP- pulps.

Consideration of Handsheet Data

Handsheet data obtained by the procedures noted in the experimental part for Pulps OO-1, OO-3, OO-2, and OO-4 may be considered as a group. In each of the following graphs, all data for any one pulp are plotted using the symbols shown in Table XI.

Figure 14 shows beating time versus Canadian freeness, from which it will be observed that the pulps are ranked so that greater yield coincides not only with less sensitivity to beating but also to a greater freeness range. When compared with data from the laboratory kraft reference pulp in Table V, which includes beating times to 600, 500, 400, 300, and 200 Canadian freeness, it can be seen from Table XII that two of the OO- pulps have a freeness spread comparable to that for the kraft pulp. Pulp OO-1 reveals a new aspect of chlorine dioxide-alkali pulps. In considering this, it is noted that the kraft pulp was beaten using the normal standard procedure which calls for a 5.5-kg. weight on the end of the bedplate lever. From previous knowledge of the rapidity with which freeness of holopulps is lowered using such a procedure, the data such as in Tables IV and XII relate to beating with a 2.0-kg. weight on the end of the bedplate lever. Therefore, Pulp OO-1 differs markedly from Pulp OO-4 and the PP- pulps in that it has a significantly reduced

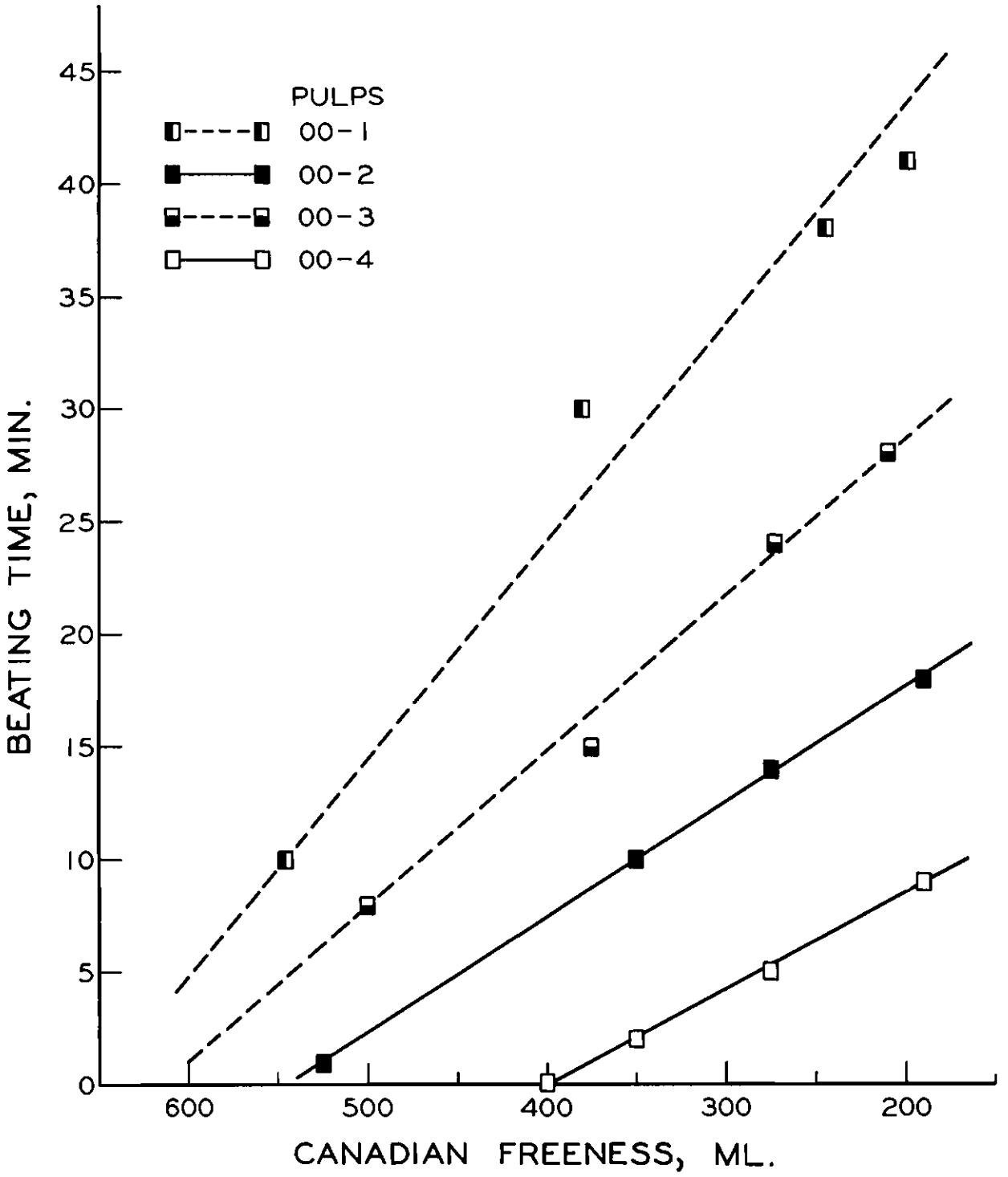

Figure 14. Beating Time in Valley Beater Versus Canadian Freeness for the 00- Pulps

TABLE XII

CANADIAN FREENESS VS. BEATING TIME FOR 00- PULPS[a]

Pulp	Canadian Freeness, ml.	Beating Time, min.
00-1 ◧	600	5
	500	16
	400	27
	300	35
	200	41
00-3 ◒	600	1
	500	8
	400	15
	300	22
	200	29
00-2 ■	500	2
	400	7
	300	13
	200	18
00-4 □	400	0
	300	4
	200	9

[a] For test details, see Experimental, Pulp Evaluation.

sensitivity to beating and apparently is more like the kraft pulp. For strict comparison, beating would need to be carried out with the same weight on the end of the bedplate lever.

The relationships of beating time to handsheet density, as in Fig. 15, show that considerable differences exist between the four pulps and that Pulp 00-1 is much less readily beaten than Pulp 00-4. In addition, the former provides handsheets with densities at the low end of the scale, whereas the latter pulp does not. Since alkali conditioning was omitted, oxidative reaction was the same, the hypochlorite reaction was the same, and only the conditions of alkali extraction have been varied in obtaining Pulps 00-1, 00-3, 00-2, and 00-4, this figure is of considerable interest. It reveals that a chlorine dioxide-alkali pulping process allows for considerable manipulation of the properties of fibers through varying only the alkali extraction step of the process. Such responsiveness to alkali at 60°C. is not found in conventional chemical pulps. It is believed to be a reflection of the fact that the fibers are closer to their natural state and have not been as significantly changed as when pulping is carried out using more severe conditions. One result is that, as shown by Table XIII, the 0.59-0.80 range of densities derivable from Pulp 00-2 handsheet data matches the range derivable from kraft handsheet data as in Table V, thereby allowing for a greater choice in terms of handsheet density than do the PP- pulps.

The procedure used to prepare the 00- pulps permits retention of hemicelluloses without both excessive sensitivity to beating and the restriction of making paper of a more dense kind. By contrast, it appears from information available on pulping with chlorates (2) for example, the pulp had drawbacks including both excessive sensitivity to beating and conversion to dense paper. In another case where a hardwood pulp was prepared in about 70% yield after cold alkali

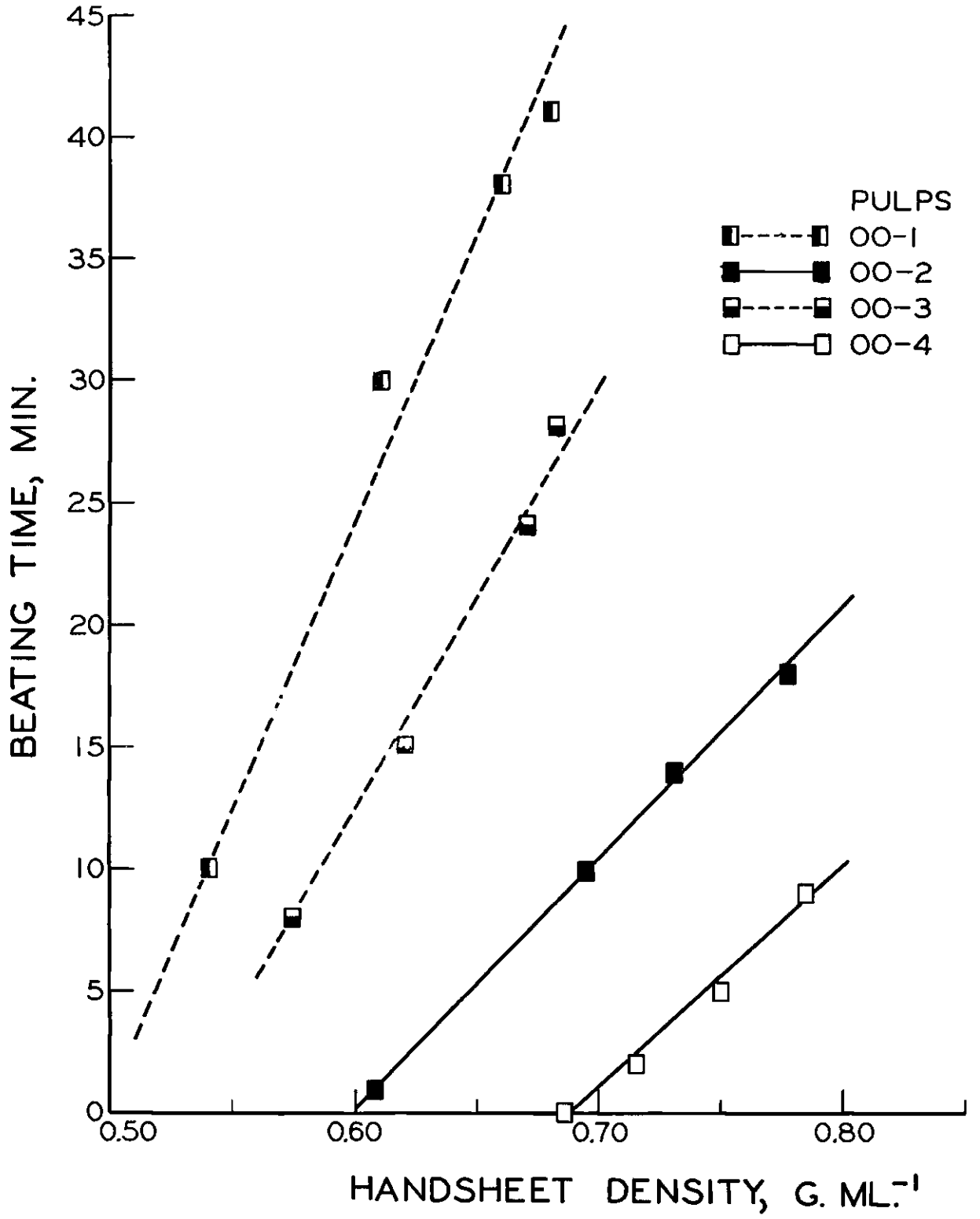

Figure 15. Beating Time in Valley Beater Versus Handsheet Density for the 00- Pulps

TABLE XIII

HANDSHEET DENSITY VS. BEATING TIME FOR OO- PULPS

Pulp		Handsheet Density, g./cc.	Beating Time, min.
OO-1	◧	0.59	22
		0.65	36
		0.69	45
OO-3	◒	0.59	11
		0.65	19
		0.69	28
OO-2	■	0.59	0
		0.65	5
		0.69	9
		0.75	16
		0.80	21
OO-4	□	0.69	0
		0.75	6
		0.80	10

extraction of chlorite holocellulose prepared from shavings (3), the handsheet density range was 0.61-0.79 and corresponded to the Canadian freeness range 275-19. The respective ranges for a kraft pulp from the same wood were 0.36-0.52 and 695-443, which are significantly different.

In the alkali extraction step, temperature has already been identified as being related to the rate of removal of modified lignin, time has already been identified as influencing fiber properties, and now concentration as reflected by pH, as recorded in Table IX, also appears to influence fiber properties. Since time and concentration together affect yield, the more precise nature of chemical and physical aspects of differences in fiber properties remains to be elucidated.

To determine further how differences in fiber properties influence handsheet properties, consideration may be given to Fig. 16-24 in which handsheet density is plotted versus the following:

Fig. 16: opacity, %,

Fig. 17: burst factor and z-tensile, kg. $cm.^{-2}$,

Fig. 18: breaking length, km.,

Fig. 19: tensile energy absorption, g. cm. $cm.^{-2}$,

Fig. 20: stretch, %, and tensile stiffness, kg. $cm.^{-1}$,

Fig. 21: Elmendorf tear factor and in-plane tear, g. cm. $cm.^{-1}$,

Fig. 22: Elmendorf tear factor x yield/65,

Fig. 23: zero-span breaking length x yield/65, km., and zero-span breaking length, km.,

Fig. 24: M.I.T. fold.

Examination of Fig. 16 reveals that the two pairs of Pulps 00-1/00-3 and 00-2/00-4 have two distinct opacity ranges, the upper one of which corresponds to alkali extraction with 6.0% sodium hydroxide. The lower opacity range corresponds to that for the PP- pulps in Fig. 4. It appears that opacity is not being influenced by time of alkali extraction, but is probably being affected by alkali concentration as reflected by pH since in the alkali extraction of Pulps PP-1, PP-2, PP-3, PP-4, 00-2, and 00-4, the final pH was 11.9 to 11.4, whereas it was 10.9 after 10 min. and 9.3 after 120 min. for Pulps 00-1 and 00-3, respectively. Some uncertainty exists in reaching the above tentative conclusion because the various pulps have different brightnesses. On the other hand, Pulps 00-1 and 00-3 have 69.0 and 70.5 brightnesses, which are about comparable to brightnesses of 66.0 and 71.0 for Pulps PP-1 and PP-3; so, at least for these, brightness effects should be minimized, thereby reducing some of the uncertainty. In future work, determination of scattering coefficients could be justified.

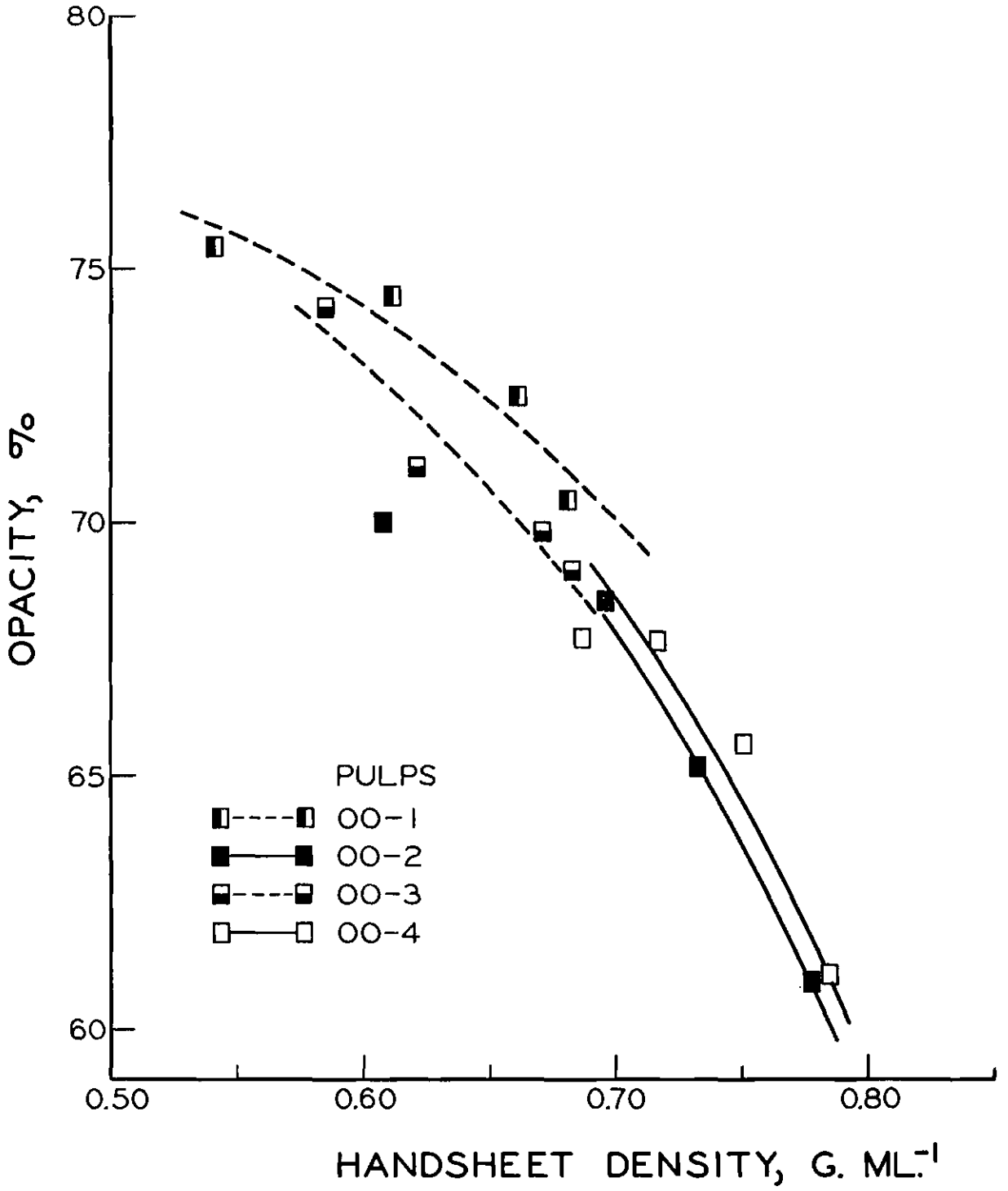

Figure 16. Relationship Between Opacity of 60-g.s.m. Handsheets and Handsheet Density for the 00- Pulps

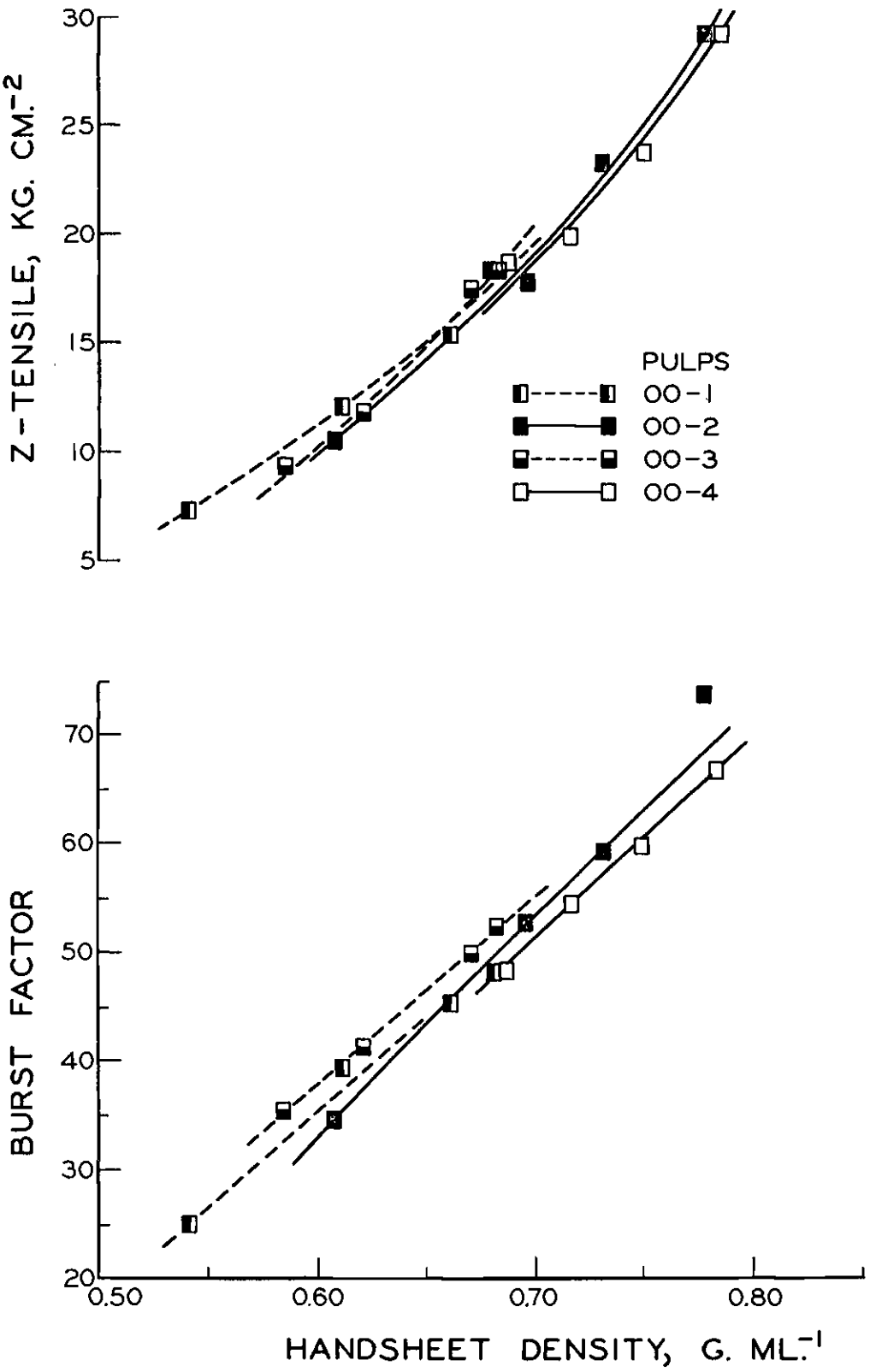

Figure 17. Effect of Handsheet Density on z-Tensile Strength and Burst Factor for the 00- Pulps

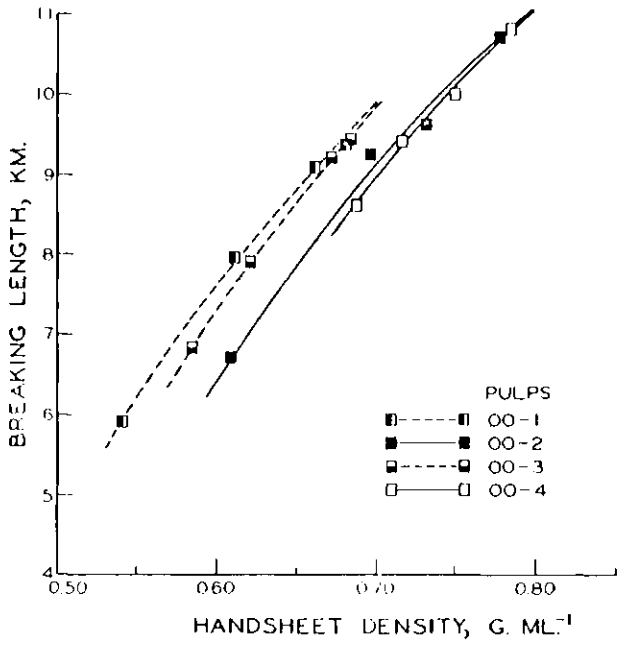

Figure 18. Relationship Between Breaking Length and Handsheet Density for the 00- Pulps

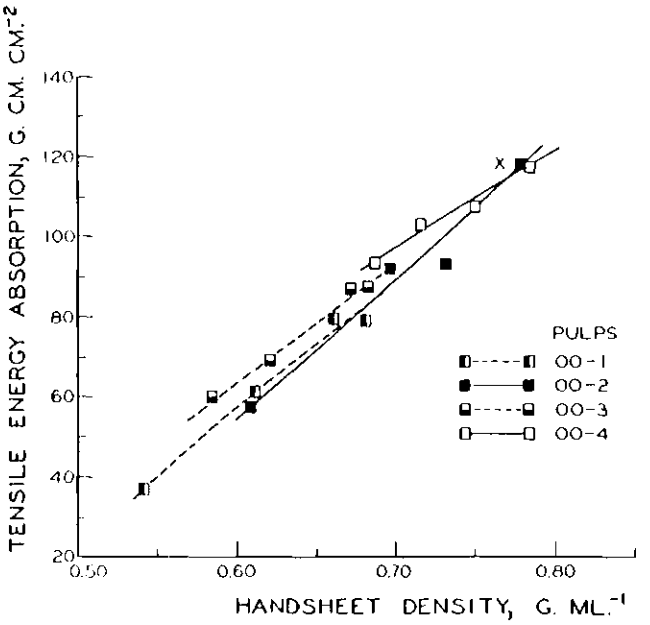

Figure 19. Relationship Between Tensile Energy Absorption and Handsheet Density for the 00- Pulps

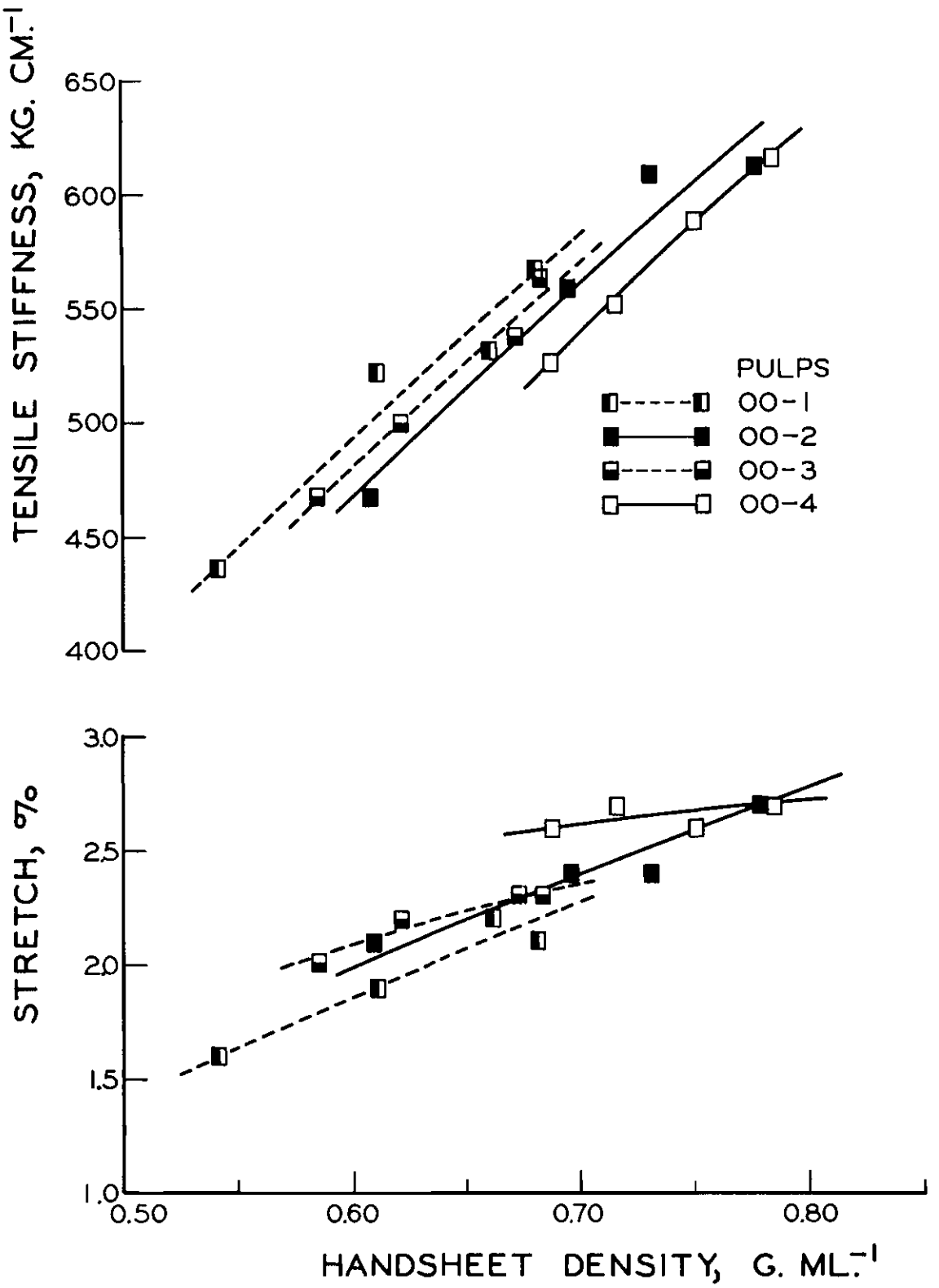

Figure 20. Effect of Handsheet Density on Tensile Stiffness and Stretch for the 00- Pulps

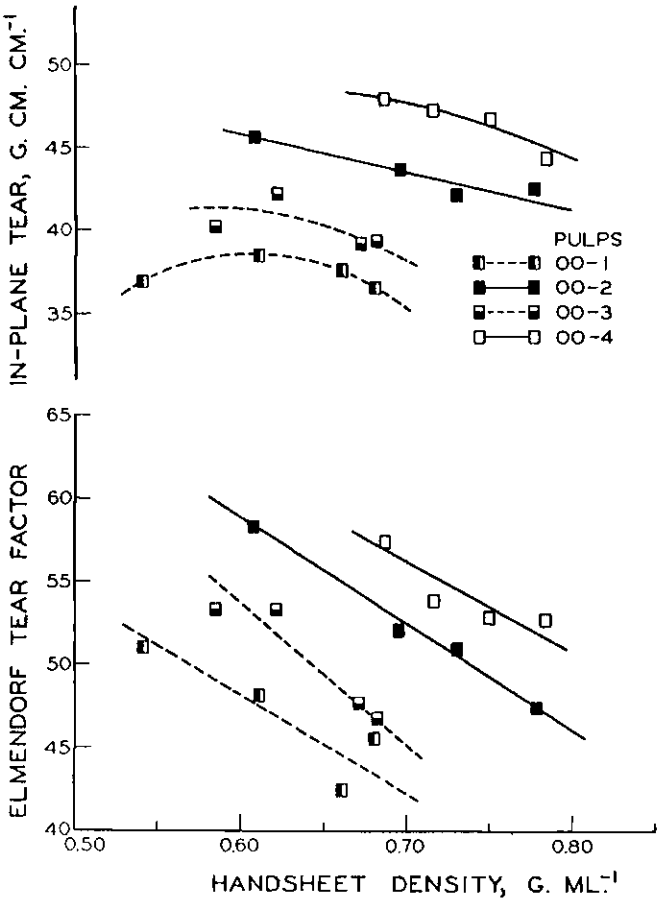

Figure 21. Effect of Handsheet Density on In-Plane Tear and Elmendorf Tear Factor for the 00- Pulps

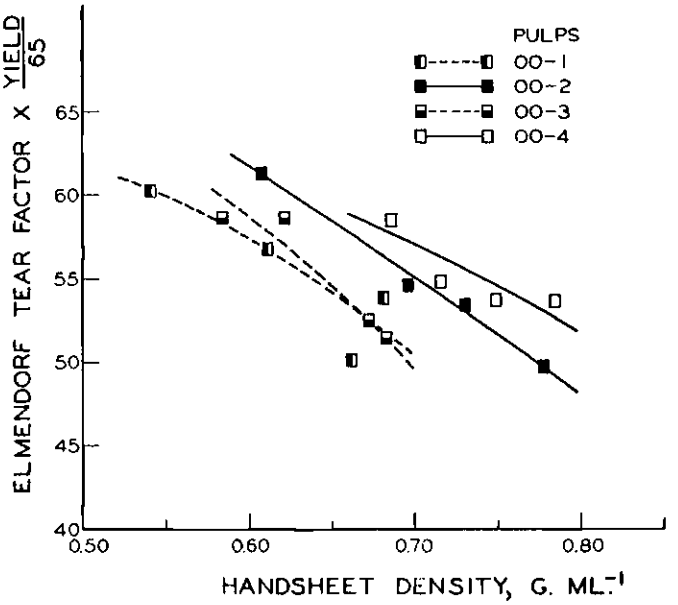

Figure 22. Relationship Between Elmendorf Tear Factor x Yield/65 and Handsheet Density for the 00- Pulps

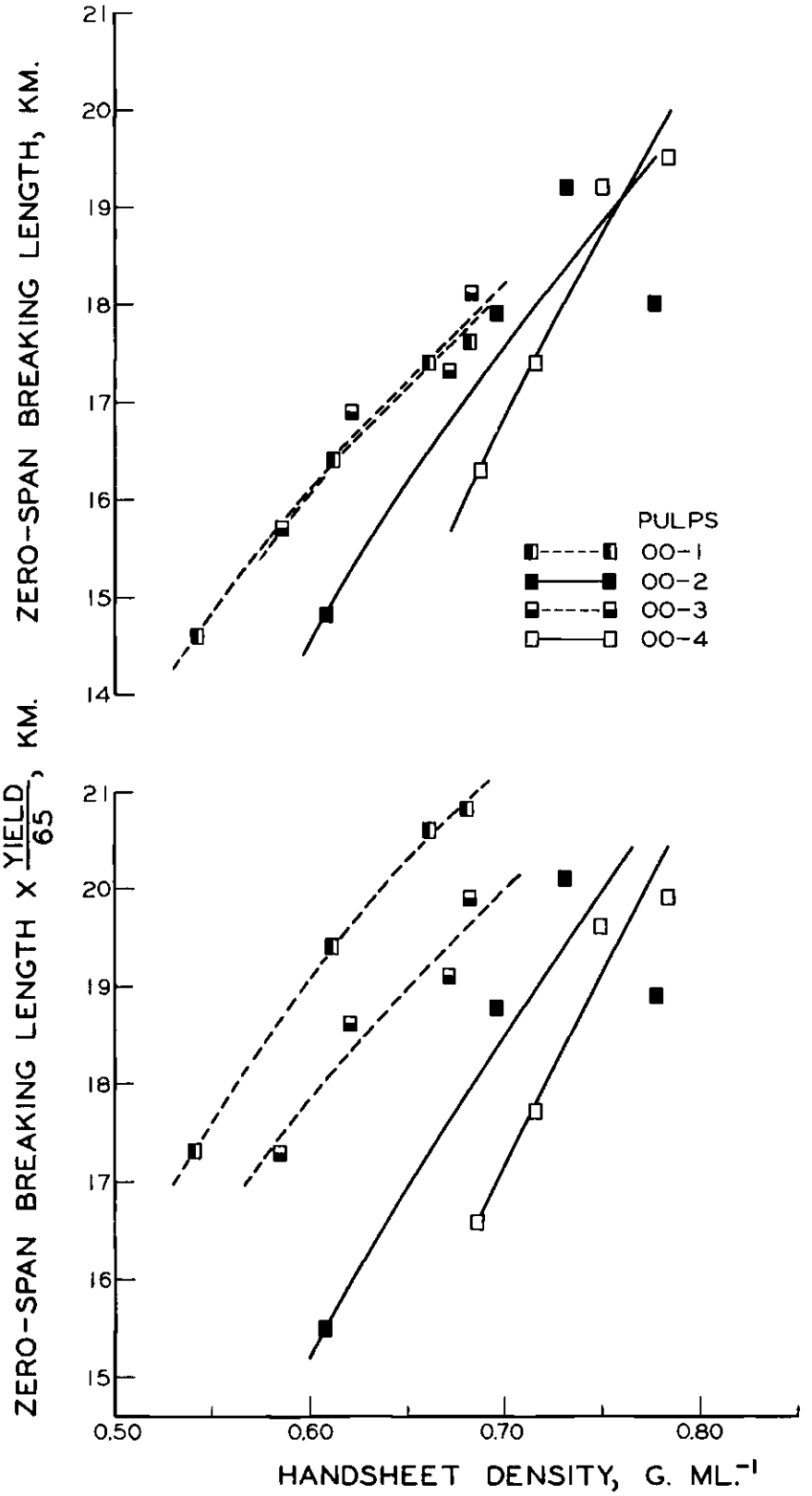

Figure 23. Effect of Handsheet Density on Zero-Span Breaking Length and Zero-Span Breaking Length x Yield/65 for the 00- Pulps

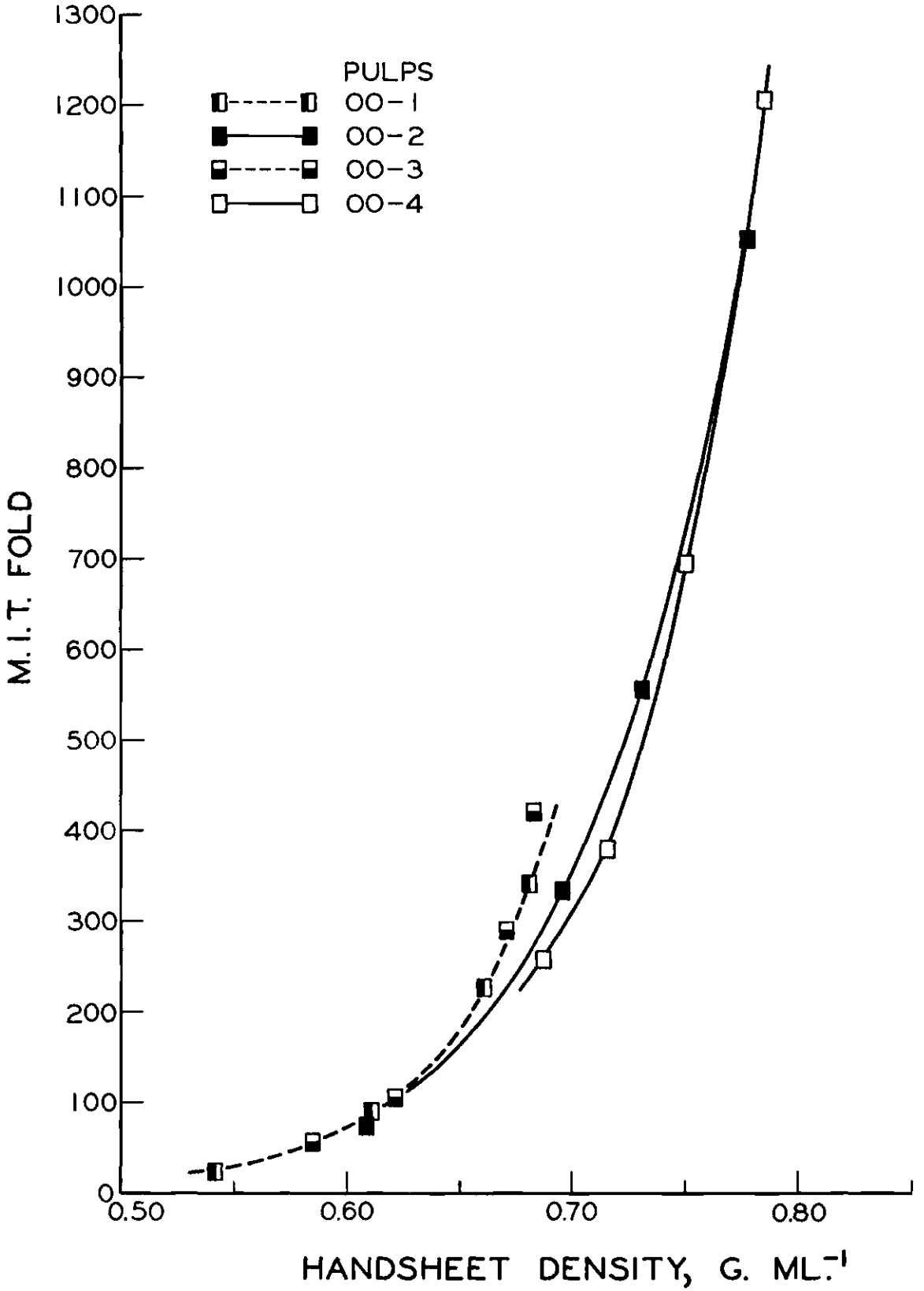

Figure 24. Relationship Between M.I.T. Fold and Handsheet Density for the 00- Pulps

From Fig. 17, 18, 19, and 20 it can be seen that burst factor, z-direction tensile, breaking length, tensile energy absorption, tensile stiffness, and stretch data for the four OO- pulps show some differences and as a generalization, Pulp OO-2 tends to rank most favorably. In Fig. 21, Elmendorf tear factor and in-plane tear data for the four pulps are well separated, although the separation of tear factor data is diminished where adjusted for yield differences, as in Fig. 22. Zero-span breaking lengths, as in Fig. 23, increase markedly for all pulps and reach about the same maximum value when adjusted for yield difference. The relatively steep slope of the curves in Fig. 23 is thought to reflect an increasing degree of separation into individual fibers as beating proceeded. From Fig. 24 it will be apparent that M.I.T. fold data for Pulp OO-2 cover a significantly wider range than for the other pulps.

Thus, by taking into account previous indications that lessening the extent of exposure to alkali is apparently associated with a desirable shift in fiber properties, the basis of knowledge of the potential versatility of chlorine dioxide-alkali pulping has been broadened. While with omission of alkali conditioning, nonuniformity of chemical reaction is apparently increased, the ability to markedly influence fiber properties during alkali extraction at 60°C. by changing not only time but also total alkali has been demonstrated. A direct comparison of the PP- pulps and OO- pulps follows.

COMPARISON OF CHLORINE DIOXIDE-ALKALI PULPS WITH AND WITHOUT ALKALI CONDITIONING, AND ALL HANDSHEET DATA

DISCUSSION

Introductory Comment

In the preceding parts of this report, consideration was given to four PP- pulps and four OO- pulps. From study of these two groups it appeared that omission of alkali conditioning resulted in some significant changes, especially in the properties of fibers as obtained after three further processing steps. This raises the question of whether such changes do in fact stem back to the omission of alkali conditioning, and this calls for establishing an acceptable basis for legitimate comparison in greater detail.

Selection of PP- and OO- Pulps for Comparison

From an examination of the data for the preparation of the PP- and OO- pulps in Tables II and X, respectively, it may be seen that Pulps PP-1 and PP-3 differ from the OO- pulps in that only 1.5% available chlorine was used compared with 4.5%. On this basis, and especially in view of the observed influence of varying amounts of hypochlorite on fiber properties as illustrated by Fig. 1, Pulps PP-1 and PP-3 have been dropped in making comparisons with the OO- pulps. In this group, Pulps OO-1 and OO-3 differ from those remaining not only in that the final pH during alkali extraction was lower but also in that yield and lignin content before reaction with hypochlorite were both significantly greater. Thus, Pulps OO-1 and OO-3 have also been dropped in selecting pulps for comparison. To provide a single view of the procedures used to prepare the pulps remaining, namely PP-2, PP-4, OO-2, and OO-4, the relevant data are given in Table XIV.

TABLE XIV

SUMMARY OF PREPARATION OF PULPS FOR COMPARISON

Pulp	NaOH,[a] %	ClO_2, %	OCl^-, % av. Cl_2	Consistency, %	Temp., °C.	Time, min.	Final pH	Yield, %	Rejects, % o.d.p.	Klason + Acid-sol. Lignin, %	GE Brightness	Canadian Freeness (5 min.)[b]
Alkali conditioning												
PP-2, PP-4	3.0	--	--	6.0	50	60	10.5	94.6	--	--	--	--
00-2, 00-4	nil											
Oxidative reaction												
PP-2, PP-4	3.5	9.0	--	5.0	25/35	270	3.0	89.2	--	--	--	--
00-2, 00-4	3.5	9.0	--	6.0	25/35	295	2.6	94.9	--	--	--	--
Alkali extraction												
PP-2	6.0	--	--	8.0	60	10	11.6	71.5	--	5.2	--	--
00-2	9.0	--	--	8.0	60	10	11.9	72.3	--	7.7	--	--
PP-4	6.0	--	--	8.0	60	120	11.4	67.6	--	3.7	--	--
00-4	9.0	--	--	8.0	60	120	11.7	67.7	--	5.5	--	--
Hypochlorite												
PP-2	0.25	--	4.5	12.0	40	245	7.7	67.1	0.9	2.2	75.5	490
00-2	0.25	--	4.5	12.0	40	180	7.9	68.2	9.0	4.5	74.0	580
PP-4	0.25	--	4.5	12.0	40	>270	7.9	63.1	0.3	1.4	78.0	405
00-4	0.25	--	4.5	12.0	40	235	7.9	66.2	4.4	3.0	77.5	460

[a] All data on ovendry fiberized chip basis unless noted otherwise.

[b] After circulation for 5 min. in Valley beater with no bedplate load.

The experimental parameters give recognition to a number of factors previously found to have some influence. For example, the conditions of reaction with hypochlorite are identical except for some variation in time that can be related to lignin content after alkali extraction. Alkali extraction is at 60°C., for rapid removal of modified lignin, and for 10 and 120 min. to detect the influence of carbohydrate changes on fiber properties. Final pH values after alkali extraction are close together to minimize the effect of alkali concentration. After alkali extraction, the two pairs of pulps, PP-2/00-2 and PP-4/00-4, have within-pair differences related to whether or not alkali conditioning preceded oxidative reaction and a between-pair difference concerned with time of extraction. It will be noted that the within-pair yields are practically identical, but there is a little more lignin in the pulps not alkali conditioned. On the whole, these four pulps appear to provide a reasonable basis for endeavoring to isolate the influence of alkali conditioning under the conditions recorded.

Consideration of Handsheet Data

Figure 25 shows beating time versus both Canadian freeness and handsheet density. It would appear that beating time is particularly related to alkali extraction time at lower freenesses which exhibit no within-pair (alkali conditioning) differences. At highest freenesses, with a short alkali extraction time, alkali conditioning can result in a lower initial freeness. This probably results, at least in part, from a greater degree of separation into individual fibers. Handsheet density, as measured by TAPPI Standard Method T 220 m-60, is apparently influenced not only by alkali conditioning but also by alkali extraction time.

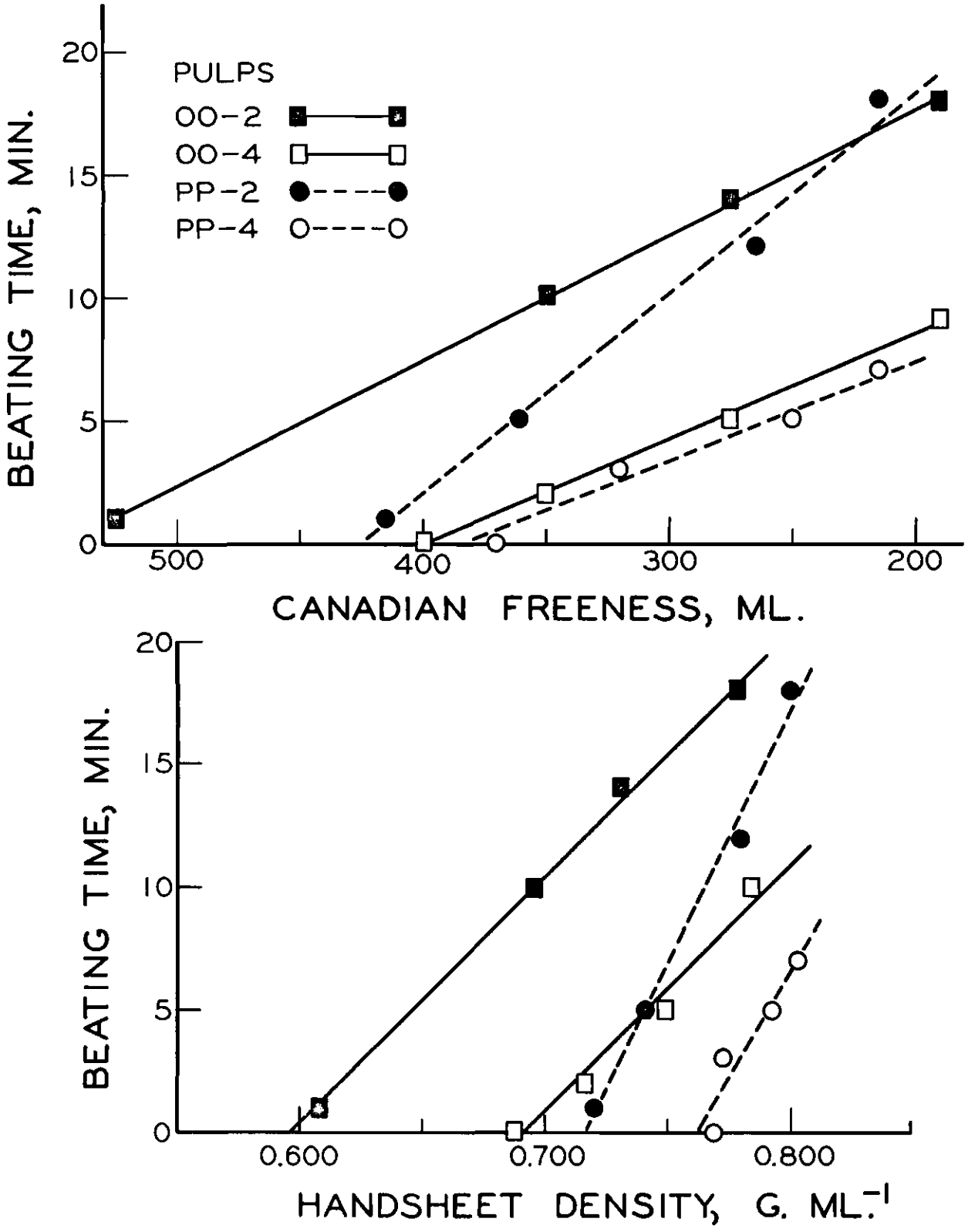

Figure 25. Beating Time in Valley Beater Versus Canadian Freeness and Handsheet Density for Selected 00- and PP- Pulps

Figures 26-29, like Fig. 25, are concerned only with the selected pulps, PP-2/00-2 and PP-4/00-4, to permit identification of the influence of alkali conditioning and/or alkali extraction time when handsheet density is plotted versus the following:

Fig. 26: breaking length, km.,

Fig. 27: stretch, %, tensile stiffness, kg. $cm.^{-1}$, and tensile energy absorption, g. cm. $cm.^{-2}$,

Fig. 28: Elmendorf tear factor and in-plane tear, g. cm. $cm.^{-1}$,

Fig. 29: zero-span breaking length, km., and M.I.T. fold.

Figure 26 illustrates quite well how breaking length has been favorably influenced by omission of alkali conditioning. Tensile energy absorption and tensile stiffness have also shown a desirable shift, although tearing properties reveal no marked change, as seen from Fig. 27 and 28, respectively.

The zero-span breaking length and M.I.T. fold data in Fig. 29 are of particular interest. First, it will be obvious that better results were obtained without alkali conditioning, but perhaps more important is consideration of why this is so. It will be observed that Pulp PP-4 was significantly inferior to the others. Table XIV shows through the hypochlorite data that of the four pulps obtained, PP-4 is the one most likely to have been degraded by hypochlorite. With pulps of this kind, the presence of noncellulosic carbohydrates makes viscosity measurements of very doubtful value as an indication of pulp degradation. Recent studies on the permanence and durability of paper (4) are consistent with M.I.T. fold and zero-span tensile strength being indicative of the extent of degradation. In the present work, these measurements should also provide a guide to the extent of degradation. Thus, it is concluded that Pulp PP-4 has been degraded. The question arises as to whether the same applies to Pulp PP-2. To check this point, it is logical to consider Pulps PP-1 and -3 since one third of the amount of

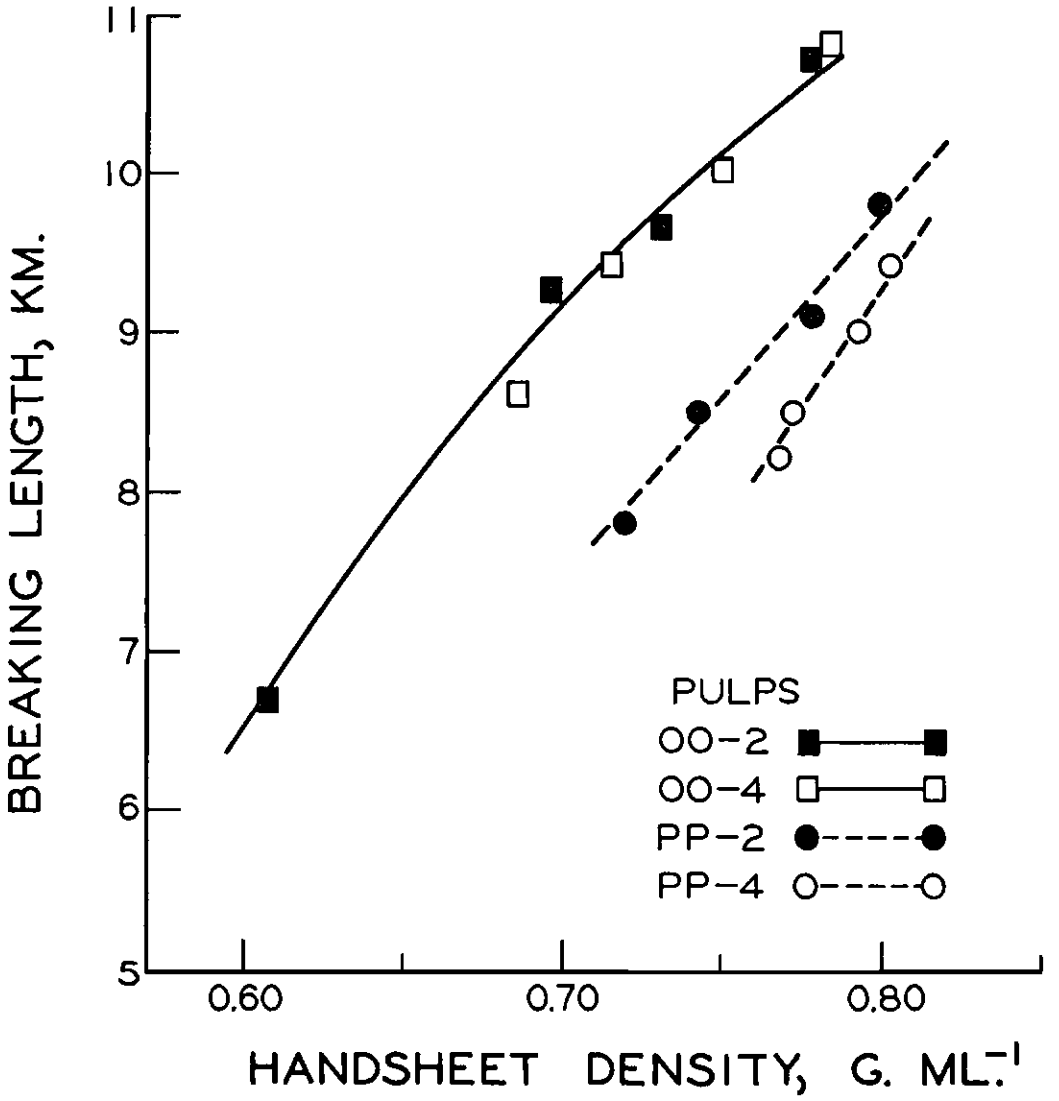

Figure 26. Effect of Handsheet Density on Breaking Length for Selected OO- and PP- Pulps

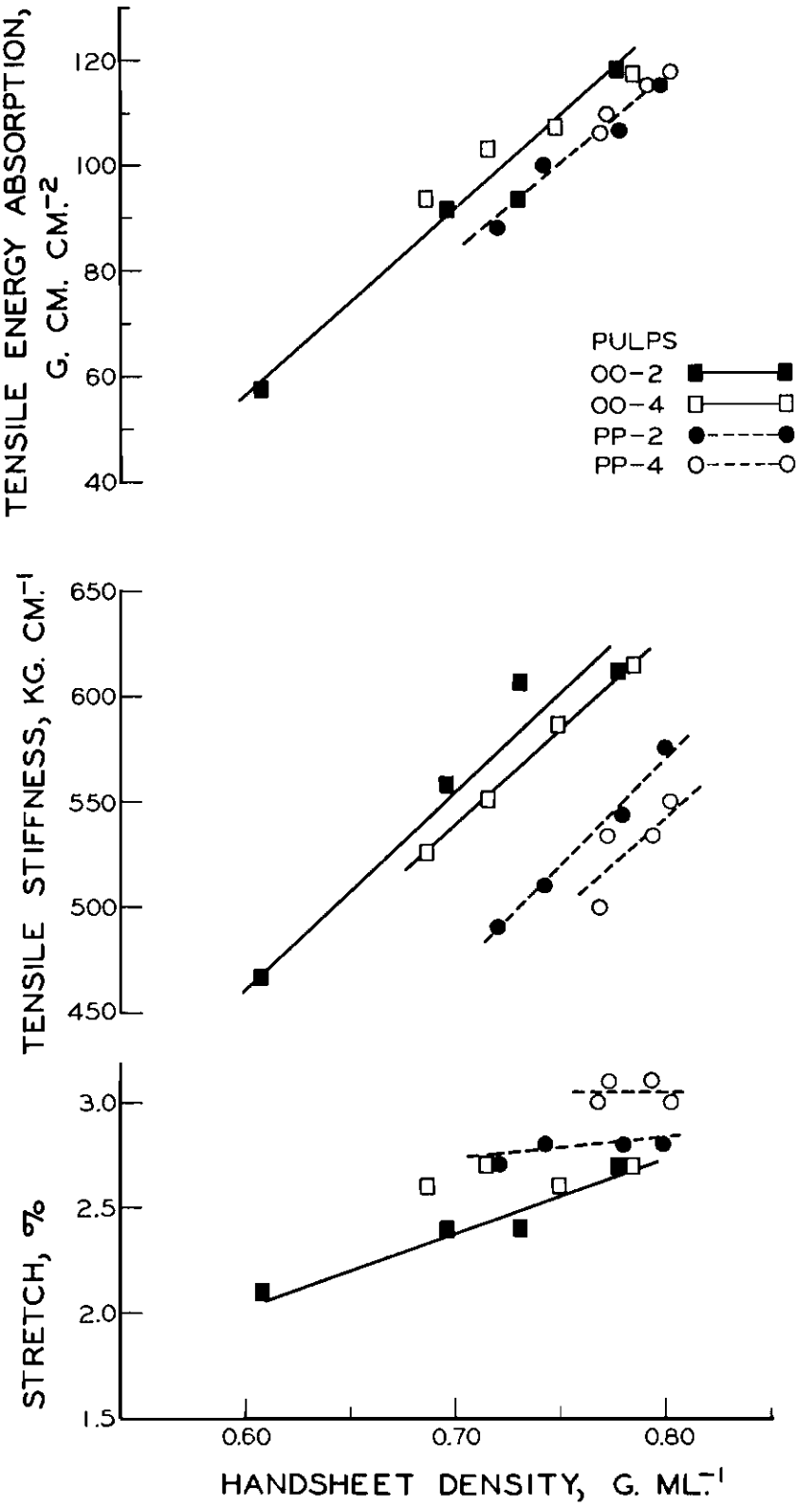

Figure 27. Effect of Handsheet Density on Tensile Energy Absorption, Tensile Stiffness, and Stretch for Selected 00- and PP- Pulps

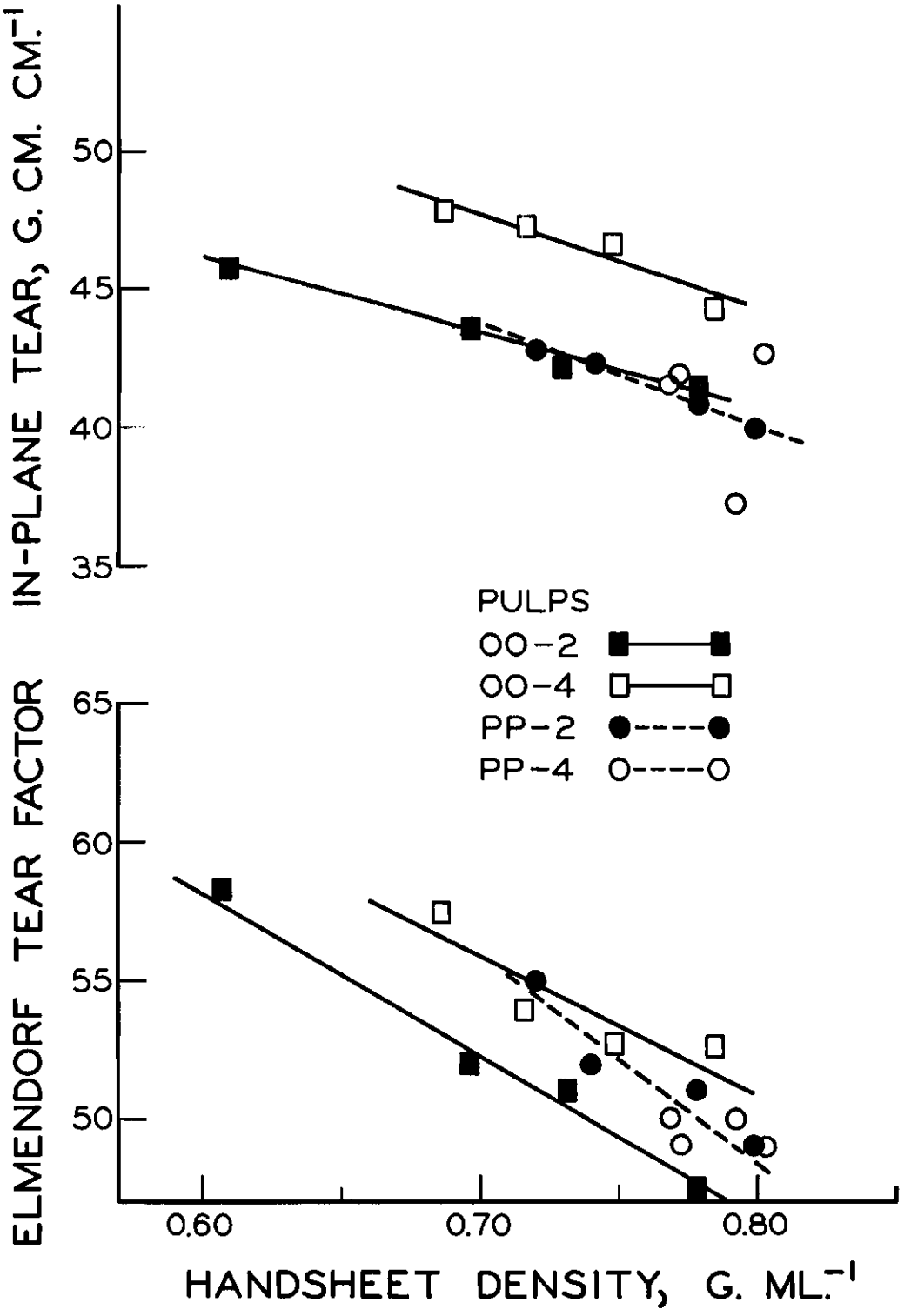

Figure 28. Effect of Handsheet Density on In-Plane Tear and Elmendorf Tear Factor for Selected 00- and PP- Pulps

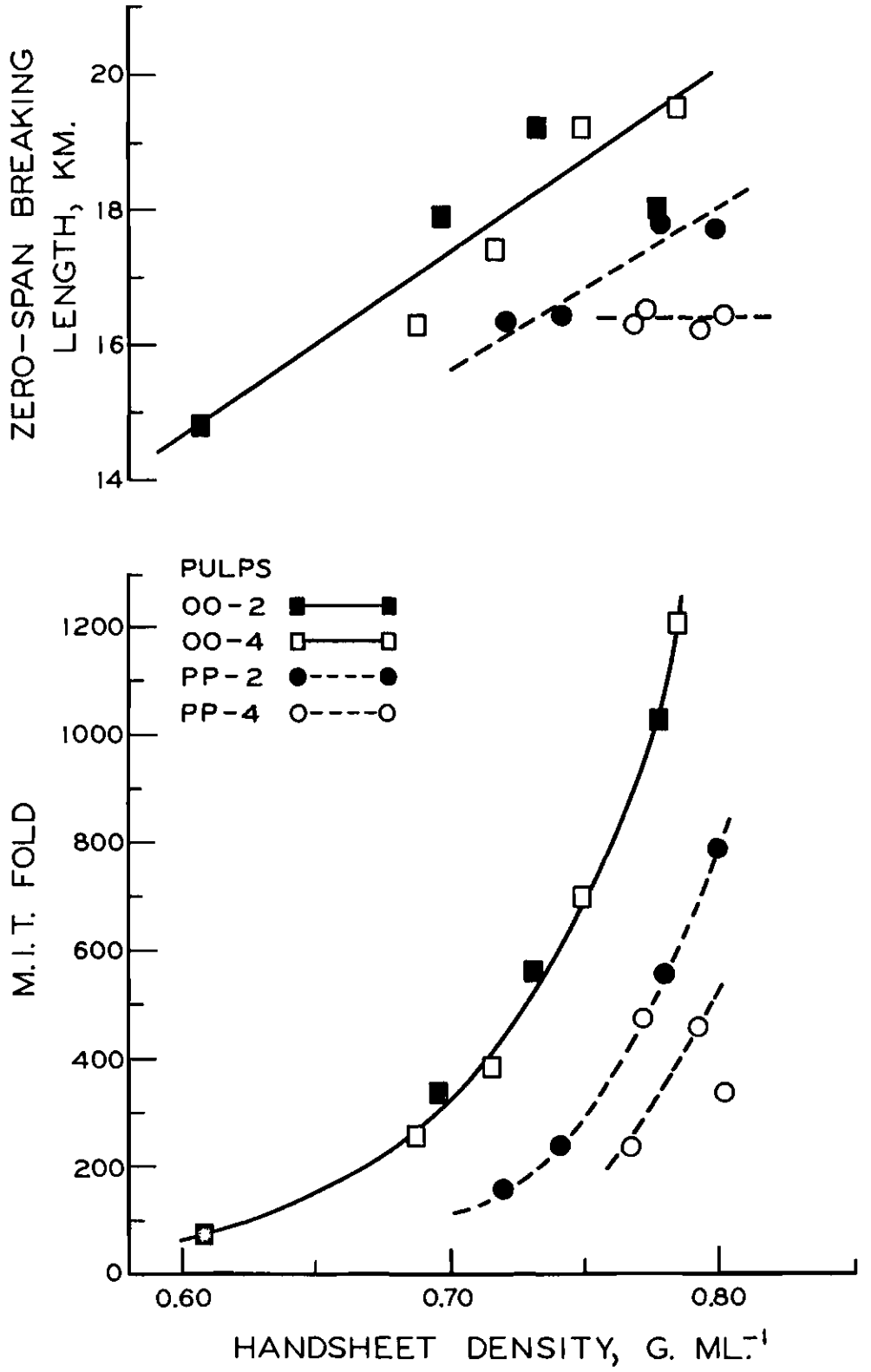

Figure 29. Effect of Handsheet Density on Zero-Span Breaking Length and M.I.T. Fold for Selected OO- and PP- Pulps

hypochlorite was used in their preparation. Reference to Table III reveals the M.I.T. fold data for PP-2 are not significantly different from those for PP-3 and PP-4 which are inferior to the M.I.T. fold data for the OO-2 and OO-4 pulps. The zero-span breaking length data on a 65% yield basis for the PP-1 and PP-3 pulps are likewise inferior to the corresponding data for the OO- pulps. Thus, reduction in the amount of hypochlorite used on the PP- pulps supports the view that the better properties of the OO-2 pulps as in Fig. 29 are related to some factor in addition to any degradation by hypochlorite.

Figure 30 illustrates how after some beating the OO- pulps have a greater tensile stiffness at a given opacity than the PP- pulps, indicating once more how process differences influence sheet properties.

Excepting the fact that Pulp PP-4 apparently is degraded, it appears that omission of alkali conditioning (as detailed in Table XIV) and shorter extraction time were both associated with a desirable shift in the properties of screened fibers on the basis of handsheet data.

Selection of Pulps for Comparison Using Gaseous Oxidative Reaction

Progress Report Five, which was concerned with the addition of gaseous chlorine dioxide in the oxidative reaction, included data for an unbleached pulp, GP-4, prepared with alkali conditioning and a bleached pulp, GP-5, prepared without alkali conditioning. Tables XV and XVI show the similarities in lignin content, yield, freeness, etc. for Pulps GP-4 plus LL-10 and GP-5 plus OO-4, respectively. Comparison of these is of particular interest in determining the extent to which it might be possible to predict handsheet properties of pulps obtained by adding gaseous instead of aqueous chlorine dioxide in the oxidative reaction.

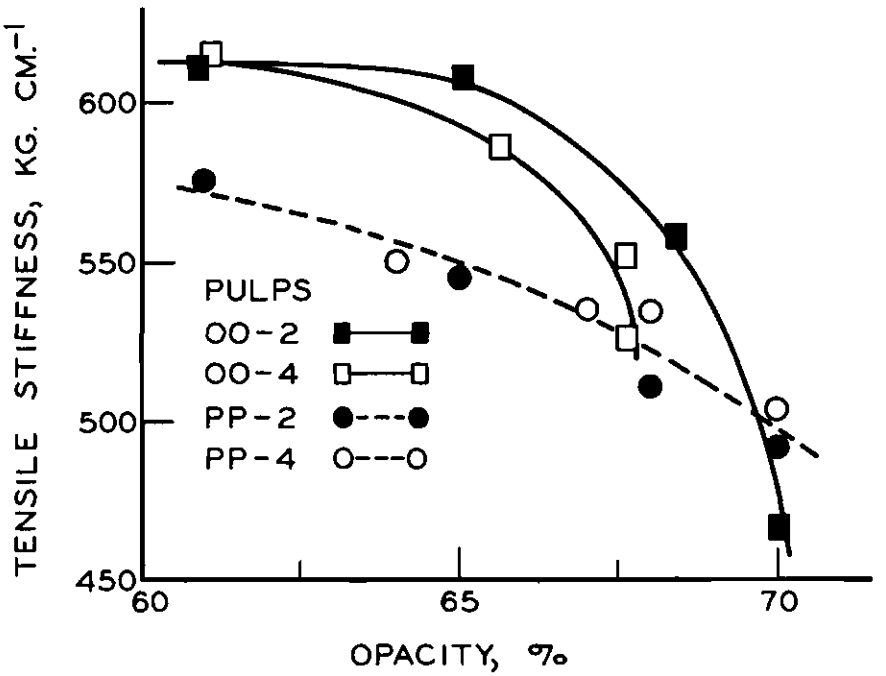

Figure 30. Relationship Between Tensile Stiffness and Opacity for Selected OO- and PP- Pulps

TABLE XV

COMPARISON OF UNBLEACHED PULPS GP-4 AND LL-10

Process Step	Alkali Conditioning		Oxidative Reaction		Alkali Extraction	
Pulp code	GP-4	LL-10	GP-4	LL-10	GP-4	LL-10
NaOH, %[a]	3.2	3.0	0	3.5	6.2	6.0
ClO_2, %	0	0	7.8[b]	9.0	0	0
Consistency, %		6.0	--[c]	5.0	N.A.	8.0
Temperature, °C.	60	50	25-36[d]	25/35	50	50
Time, min.	60	60	10-20	270	60	10
Final pH		10.5		3.0		11.8
Yield, %		96.4		90.7	73	73.0
Rejects, % o.d. pulp	--	--	--	--	15	7.0
Klason + acid-sol. lignin, %	--	--	--	--	9.7	9.6
Yield - lignin, %	--	--	--	--	63.3	63.4
GE brightness	--	--	--	--	30	N.A.
Canadian freeness (5 min.)[e]	--	--	--	--	555	560

[a] All percentages are based on original o.d. fiberized chips.

[b] Two-stage oxidation, split 6.1/1.7.

[c] Gaseous-phase reaction.

[d] Exit gas temperature.

[e] After circulation in Valley beater for 5 min. with no bedplate load.

TABLE XVI

COMPARISON OF PULPS GP-5 AND 00-4

Process Step	Oxidative Reaction		Alkali Extraction		Hypochlorite	
Pulp code	GP-5	00-4	GP-5	00-4	GP-5[a]	00-4
NaOH, %[b]	0	3.5	9.0	9.0	--[c]	0.25
ClO_2, %	9.3	9.0	0	0	0	0
OCl^-, % av. Cl_2	0	0	0	0	2.5	4.5
Consistency, %	--[d]	6.0		8.0	8	12
Temperature, °C.	40-45[e]	25/35	60	60	40	40
Time, min.	10-20	295	60	120	180	235
Final pH	--[f]	2.6	--	11.7	10.6	7.9
Yield, %		94.9	68	67.7	64	66.2
Rejects, % o.d. pulp	--	--	4	--	--	4.4
Klason + acid-sol. lignin, %	--	--	5.7	5.5	2.7	3.0
GE brightness	--	--	43.7	--	80	77.5
Canadian freeness, 5 min.[g]	--	--	505	--	405	460

[a] Only screened portion treated subsequent to alkali extraction step.

[b] All percentages based on original o.d. fiberized chips.

[c] Some NaOH added to maintain high pH.

[d] Gaseous-phase reaction.

[e] Exit gas temperature.

[f] In GP-5 fiberized chips (2.3 kg. o.d.) with 51% moisture content, after reaction with chlorine dioxide were collected at the reactor exit in a plastic bag. As moisture accumulated, it was transferred from time to time into a tank of cold water. When all the reacted material had been transferred to the tank which contained roughly 200 liters of water, the pH was 2.0. The dilution factor is therefore about 200/2.3, or about 87. If the pH before dilution is obtained by extrapolation, it would be: pH after dilution - log (dilution factor) = 2 - approx. $1.94 \approx 0.05$.

[g] After circulation in Valley beater for 5 min. with no bedplate load.

For Pulps GP-4 and LL-10, although different lots of chips were used, the method of fiberization was the same, and about the same conditions were followed for both alkali conditioning and alkali extraction, as shown in Table XV. For the oxidative reaction when gaseous chlorine dioxide was added to moist, fiberized chips, the reaction proceeded more rapidly than when aqueous chlorine dioxide was used. For Pulps GP-5 and OO-4, there were some differences in the alkali extraction and hypochlorite reaction conditions. However, the selection made represents about the best match of these conditions, and again, when gaseous chlorine dioxide was added to moist, fiberized chips, the reaction proceeded more rapidly than when aqueous chlorine dioxide was used. The relatively rapid reaction of gaseous chlorine dioxide with moist pulp also has been observed, for example, in some bleaching experiments (5).

Consideration of Handsheet Data

The handsheet data for Pulps GP-4 and LL-10 are compared in Fig. 31 and show a remarkably close similarity. For Pulps GP-5 and OO-4, the corresponding comparison is presented in Fig. 32. In this, the most notable differences occur in tear factor and breaking length. It is uncertain why these are significantly greater for Pulp GP-5. Variation between different lots of chips could provide an explanation since, in kraft pulping studies on aspen, between-tree variations of 70 to 90 and 10,500-14,000 meters have been found for tear factor and breaking length, respectively. Other properties of handsheets from Pulps GP-5 and OO-4 are similar. It will be recalled that Pulp OO-2 has a higher freeness and is slower beating than Pulp OO-4.

With the information currently in hand, it is tentatively concluded that the oxidative reaction can be carried out either by the use of gaseous chlorine

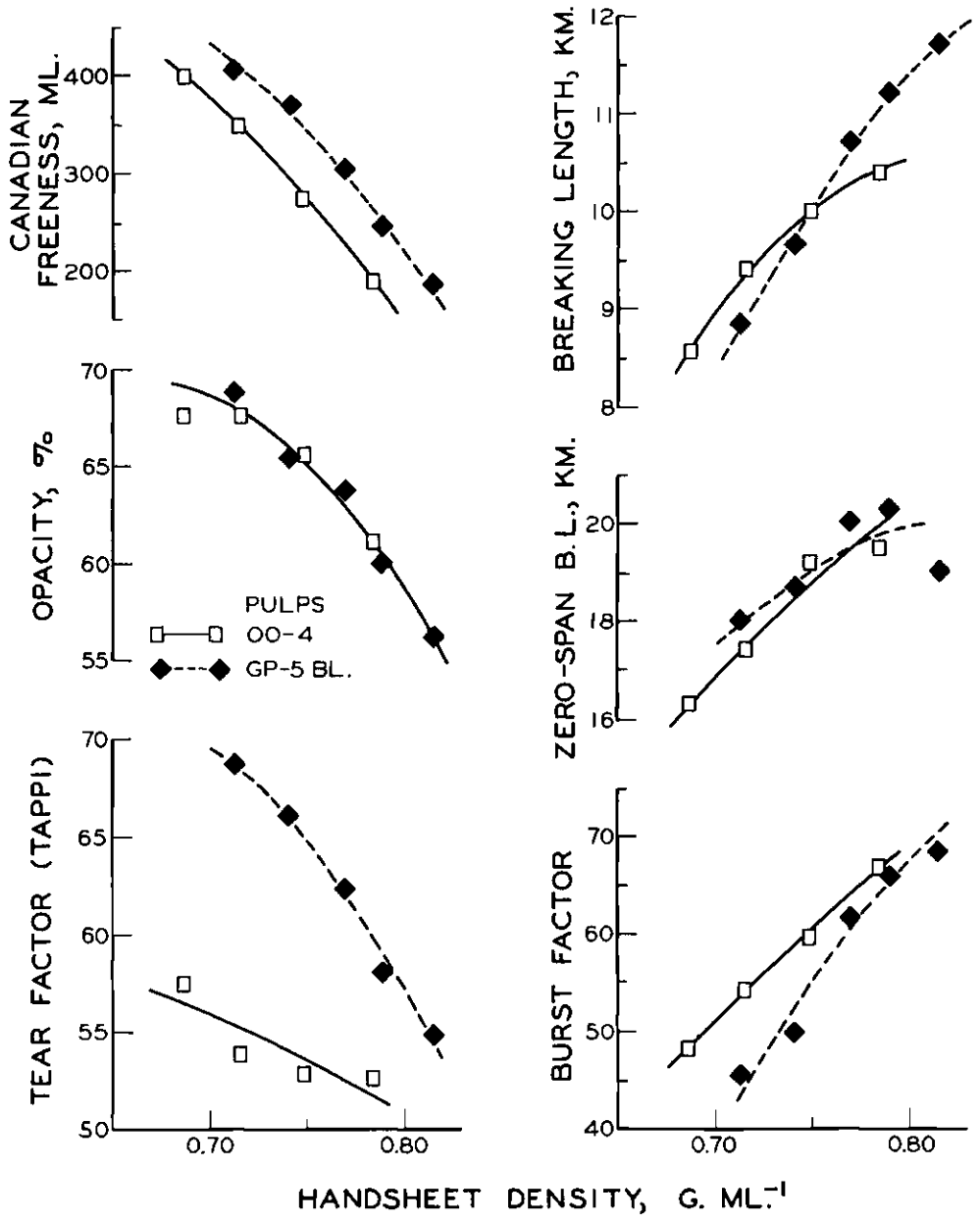

Figure 31. Freeness and Handsheet Properties Versus Handsheet Density. Comparison of Unbleached Pulp LL-10 Prepared Using Aqueous Chlorine Dioxide with Unbleached Pulp GP-4 Prepared Using Gaseous Chlorine Dioxide

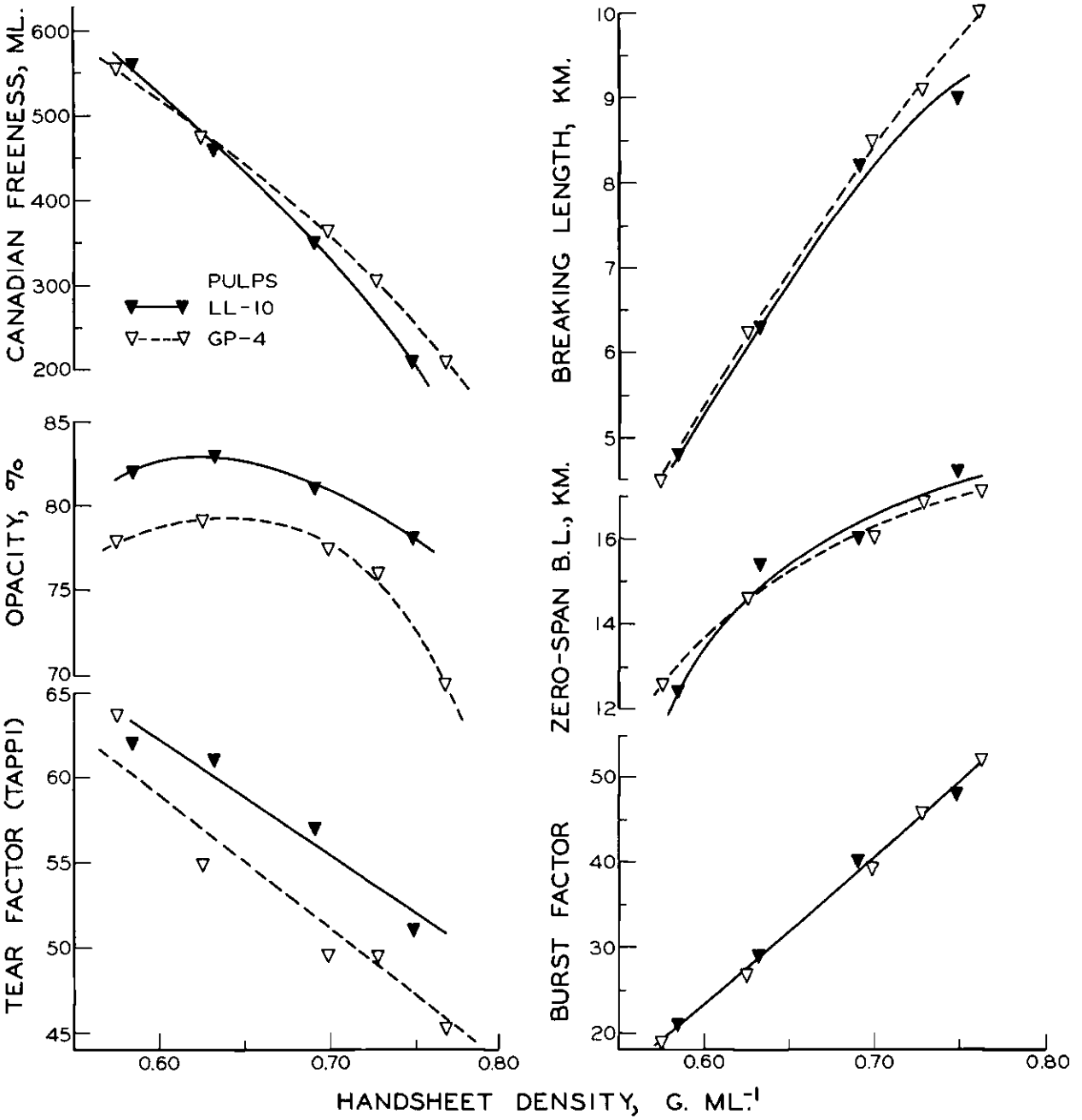

Figure 32. Freeness and Handsheet Properties Versus Handsheet Density. Comparison of Bleached Pulp 00-4 Prepared Using Aqueous Chlorine Dioxide and Bleached Pulp GP-5BL Prepared Using Gaseous Chlorine Dioxide

dioxide or aqueous chlorine dioxide to give pulps with about the same properties. Other factors play a more significant role in causing changes in fiber properties.

Comparison of All Handsheet Data for PP- and OO- Pulps

Graphs based on the data in Table III for the PP pulps, Table V for an unbleached kraft pulp, and Table XI for the OO- pulps were used to derive handsheet properties at both similar densities and similar freenesses.

In Table XVII handsheet data at TAPPI sheet densities of 0.59, 0.65, 0.69, 0.75, and 0.80 g./cc. are compared.

Generally speaking, in the past holocellulose-type pulps have been recognized as having limitations characterized by a tendency to beat rapidly to low freeness with the provision of relatively dense, well-bonded handsheets having a low opacity. From Table XVII it will be clear that such limitations no longer apply.

Pulp OO-1, for example, beat somewhat slowly to a low freeness and developed favorable handsheet strength properties at relatively low handsheet densities. This pulp, which was obtained in the highest yield, still contained an appreciable amount of lignin, and since the yield was above the fiber liberation point, refining at high consistency would be a preferred approach to developing strength in such a case. To what extent a pulp of this type could be more fully bleached remains to be elucidated; however, it does clearly demonstrate the limitations of holocellulose-type pulps are avoidable in chlorine dioxide-alkali pulps.

Pulp OO-2 is the only pulp with the same TAPPI handsheet density range as the kraft pulp which represents the first occasion on which such a degree of versatility has been achieved during work on this project.

TABLE XVII

COMPARISON AT SIMILAR DENSITY OF HANDSHEET DATA FOR HOLOPULPS AND UNBLEACHED KRAFT PULP FROM ASPEN

Pulp	OO-1	OO-3	OO-2	Kr.	OO-1	OO-3	OO-2	Kr.	PP-1	OO-1	OO-3	OO-2	OO-4	Kr.	PP-1	PP-2	PP-3	PP-4	OO-2	OO-4	Kr.	PP-2	PP-3	PP-4	OO-2	OO-4	Kr.
Density, g./cc.	0.59[a]				0.65[a]				0.69[b]						0.75[c]							0.80[d]					
C.F., ml.	430	490	560	620	280	330	440	530	460	180	220	360	400	470	286	540	340	--	230	290	370	200	200	247	130	160	180
Beating time, min.	22	11	0	0[e]	36	19	5	5[e]	0	45	28	9	0	10[e]	18	6.5	4	--	16	6	17[e]	18	14	7.5	21	19	25[e]
Opacity, %	75	74	74	--	72	71	71	--	70	71	69	68	69	--	66	68	69	71	64	65	--	61	64	66	58	59	--
Breaking length, km.	7.4	7.0	6.1	5.4	8.8	8.6	7.8	7.1	9.7	9.7	9.6	9.9	9.7	8.2	8.8	8.5	8.0	7.5	10.2	10.1	9.5	9.9	10.0	9.6	11.1	11.0	10.4
Stretch, %	1.8	2.0	2.0	1.1	2.1	2.2	2.2	1.6	2.3	2.2	2.3	2.3	2.6	2.2	2.8	2.8	3.0	3.0	2.6	2.7	2.5	2.8	3.2	3.1	2.8	2.7	2.9
Tens. energy, abs., g.cm./cm.^{2}	55	55	55	26	77	70	70	50	68	90	90	90	90	66	104	99	100	96	108	108	90	115	133	121	123	123	118
Tens. stiffness, $\frac{Et}{kg./cm}$	480	470	460	580	540	530	510	610	485	570	560	550	530	625	541	518	495	500	600	590	645	576	547	550	540	570	660
Burst factor	34	36	31	20	44	46	43	30	36	50	53	51	49	40	51	49	46	45	63	60	52	60	59	57	72	70	60
Tear factor (Elmen.)	49	54	59	57	45	49	56	69	58	43	46	53	57	74	52	53	52	--	49	53	74	48	55	48	46	51	69
Tear factor x yld./65	58	59	62	44	54	54	58	54	62	51	51	56	57	57	56	54	58	--	52	55	58	50	56	49	48	52	54
In-plane tear, g.cm./cm.	39	41	46	--	38	40	45	--	42	36	39	44	48	--	44	42	47	43	42	46	--	40	45	39	41	44	--
Zero-span breaking length, km.	16	16	(14)	20	17	17	(16)	21	15	18	18	17	16	21	18	17	17	16	19	19	20	18	19	16	20	(20)	20
Zero-span breaking lgth. x yield/65	19	18	15	16	20	19	17	16	16	21	20	18	17	16	19	17	17	16	20	19	16	19	19	16	--	--	16
z-dir. tensile, kg./cm.^{2}	10.5	9.5	9.0	--	15	15	14	--	14	18.5	19	18	18	--	24.5	24	20.5	(22)	25	24	--	34	30	31.5	33	32	--
M.I.T. fold	66	60	55	3	180	180	165	10	95	400	400	305	270	50	560	320	280	170	725	700	290	790	960	520	1500	1500	525

[a] PP-1, PP-2, PP-3, PP-4 and OO-4 outside relevant data.

[b] PP-2, PP-3 and PP-4 outside relevant data.

[c] OO-1 and OO-3 outside relevant data.

[d] PP-1, OO-1 and OO-3 outside relevant data.

[e] Valley beater bedplate load 5.5 kg. compared with 2.0 for other pulps.

In general, perhaps one of the more interesting aspects of the data in Table XVII is the extent to which properties can be varied through changes in the pulping procedure, thereby providing the papermaker with a unique degree of flexibility in seeking a desirable combination of properties for a particular grade. As will be discussed later, it is necessary at this time, however, to exercise some degree of restraint in interpreting the handsheet density data in Table XVII due to questions about precision.

In Tables XVIII and XIX, handsheet data are compared at freenesses of 500, 400, 300, and 200. A notable feature arising from making this comparison is that at any of these freeness values the pulps had a specific ranking when arranged in order of increasing density, the order being 00-1, 00-3, 00-2, 00-4, PP-1, PP-2, PP-3, and PP-4. The corresponding unscreened yields were 76.8, 71.6, 68.2, 66.2, 69.9, 67.1, 65.8, and 63.1. At freenesses of 400, 300, and 200, there is an obvious dividing line in pulp properties which falls between the 00- pulps and the PP- pulps or those without and with alkali conditioning as detailed above. This dividing line falls at about equal density for each of these freeness levels. Inspection of the various values on either side of this line provides a convenient means of making comparisons, such as between Pulps 00-4 and PP-1, or 00-2 and PP-1, -2, and -3, and so on. Since Tables XVIII and XIX are an alternative means of presenting data that have been covered already, further discussion will be omitted.

TABLE XVIII

HANDSHEET DATA AT 500 AND 400 ML. FREENESS FOR HOLOPULPS AND UNBLEACHED KRAFT PULP[a] FROM ASPEN

Pulp	00-1	00-3	00-2	PP-1	Kraft	00-1	00-3	00-2	00-4	PP-1	PP-2	PP-3	PP-4	Kraft
Canadian freeness, ml.	500					400								
Density, g./cc.	0.56	0.59	0.62	0.67	0.67	0.60	0.62	0.67	0.69	0.71	0.73	0.73	0.76	0.73
Beating time, min.	16	8	2	0	8	27	15	7	0	5	2	0	0	15
Opacity, %	75	74	70	70	--	75	73	69	68	69	69	70	70	--
Breaking length, km.	6.6	6.8	7.1	6.1	7.8	7.7	8.0	8.4	8.7	7.5	7.9	7.0	7.9	9.3
Stretch, %	1.7	2.0	2.2	2.1	1.9	1.9	2.2	2.3	2.6	2.5	2.7	2.7	2.9	2.5
Tensile energy abs., g.cm./cm.^{2}	44	55	62	59	58	58	70	82	94	80	91	86	104	86
Tensile stiffness, kg./cm.	455	460	480	457	620	490	495	530	525	503	496	470	493	640
Burst factor	29	32	37	32	36	37	41	48	48	41	45	41	48	50
Tear factor (Elmendorf)	51	55	58	(58)	72	48	52	54	57	56	53	58	50	75
Tear factor x yield/65	60	60	60	(63)	56	57	57	57	57	60	55	59	49	58
In-plane tear, g.cm./cm.	38	41	45	(38)	--	39	42	45	48	44	43	48	41	--
Zero-span breaking length, km.	15	16	15	14	21	16	17	17	16	16	16	17	16	20
Zero-span breaking length x yield/65	18	17	16	15	16	19	18	18	17	17	17	17	16	16
z-direction tensile, kg./cm.^{2}	8	9	11	11	--	11	12	16	18	17	21	17	20	--
M.I.T. fold	30	55	95	60	25[b]	65	110	225	255	160	160	160	170	185[b]

[a] June, 1967. Standard 5.5-kg. weight on the end of the bedplate lever.

[b] Data were obtained on 15-month-old handsheets.

TABLE XIX

HANDSHEET DATA AT 300 AND 200 ML. FREENESS FOR HOLOPULPS AND UNBLEACHED KRAFT PULP[a] FROM ASPEN

Pulp	00-1	00-3	00-2	00-4	PP-1	PP-2	PP-3	PP-4	Kraft	00-1	00-3	00-2	00-4	PP-1	PP-2	PP-3	PP-4	Kraft
Canadian freeness, ml.	300									200								
Density, g./cc.	0.64	0.66	0.72	0.74	0.75	0.76	0.76	0.79	0.79	0.68	0.70	0.77	0.78	0.78	0.80	0.80	0.81	0.84
Beating time, min.	35	22	13	4	14	9	6	3	24	41	29	18	9	30	20	15	8	33
Opacity, %	73	71	66	66	67	66	68	68	--	71	68	62	62	64	60	63	64	--
Breaking length, km.	8.7	8.9	9.6	9.8	8.7	9.0	8.6	8.7	10.2	9.4	9.6	10.4	10.7	9.6	10.0	9.9	9.4	10.6
Stretch, %	2.0	2.3	2.5	2.7	2.8	2.8	3.1	3.1	2.9	2.2	2.3	2.6	2.7	2.8	2.8	3.2	3.0	3.0
Tensile energy abs., g.cm./cm.^{2}	70	82	98	106	102	104	111	111	112	82	91	110	116	124	117	136	118	134
Tensile stiffness, kg./cm.	530	530	585	575	541	535	511	530	660	570	570	620	615	564	575	545	555	670
Burst factor	43	48	57	59	50	53	50	52	59	47	52	64	66	59	61	59	56	65
Tear factor (Elmendorf)	46	49	51	54	53	51	56	50	71	43	46	48	52	50	49	55	50	61
Tear factor x yield/65	54	54	54	55	57	53	57	49	55	51	51	50	53	54	51	56	48	47
In-plane tear g.cm./cm.	38	41	44	47	45	42	47	42	--	37	38	41	45	42	40	45	39	--
Zero-span breaking length, km.	17	18	18	19	18	17	18	16	20	18	18	19	20	19	18	18	16	20
Zero-span breaking length x yield/65	20	19	19	19	19	18	18	16	16	21	20	20	20	20	19	18	16	15
z-direction tensile, kg./cm.^{2}	14	15	21	22	23	27	23	27	--	17	20	28	29	30	34	29	34	--
M.I.T. fold	150	220	465	580	460	410	420	510	670[b]	340	455	905	1125	980	880	900	260	1500[b]

[a] June, 1967. Standard 5.5-kg. weight on the end of the bedplate lever.

[b] Data were obtained on 15-month-old handsheets.

FURTHER CONSIDERATION OF HANDSHEET DENSITY DATA

DISCUSSION

Introductory Comment

In the laboratory studies described above, the pulps made into handsheets were not cleaned by aid of devices such as centricleaners. Thus, as can be seen from the backs of the handsheet tabs on the next page (Fig. 33), small raised specks can occur, in addition to which surface smoothness varies, the roughest case being for Pulp 00-1. Other workers (6) have also noted that papers made from a beaten holocellulose-type pulp suffered from the persistent presence of small shives.

Since the data in Table XVII for TAPPI handsheet densities of 0.59 g./cc. indicate an apparent uniqueness in strength properties of the 00- pulps compared with kraft, a critical examination of handsheet density data has been made.

Caliper Measurements

TAPPI Standard T 220 m-60 was followed in determining the caliper or thickness of handsheets. Recently, it was shown (7) how this can be influenced, for example, by the number of plies used in making the actual measurement, with the thickness per sheet as more sheets are used decreasing to a minimum for an infinite number of plies.

To check the credibility of thickness data on the 00- and PP- pulps, some handsheet test pieces that had been in safekeeping were used. A single-ply, then two, five, twenty, and forty-ply packs were used to obtain the values plotted in Fig. 34, which includes data on the kraft reference pulp handsheets. The beating times for these pulps are also included in Table XX, from which it can be seen that the percentage difference between sheet thickness based on measuring five compared

PP-1 24 min. PP-2 18 min. PP-3 12 min. PP-4 7 min.

OO-1 41 min. OO-3 28 min. OO-2 18 min. OO-4 9 min.

Figure 33. Handsheet Tabs of the PP- and OO- Pulps Beaten to a Canadian Freeness of 190 and 220 ml. Showing Surface Smoothness and Raised Specks on the Reverse Side

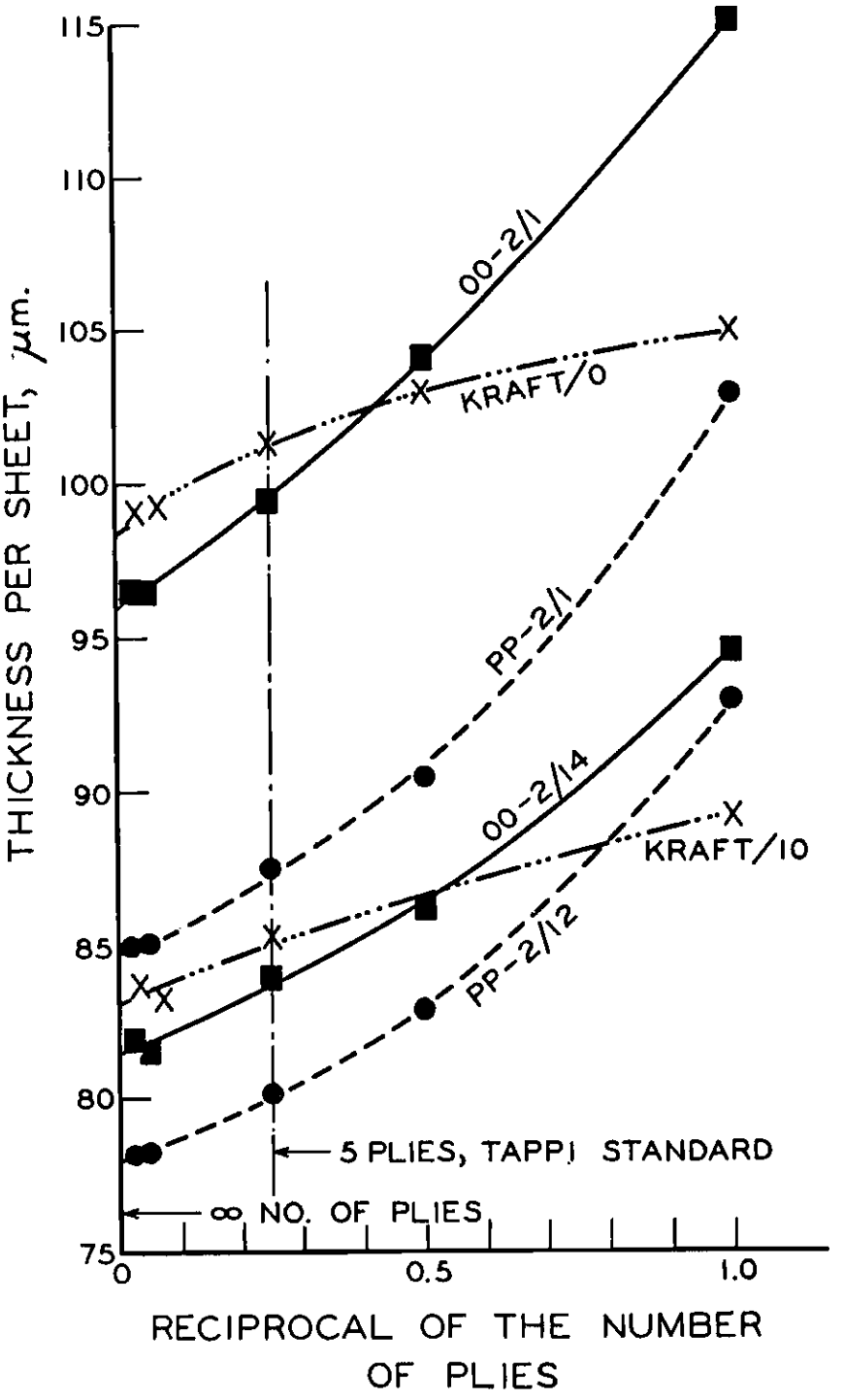

Figure 34. Effect of the Number of Plies Measured Using the TAPPI Standard Procedure on the Apparent Individual Handsheet Thickness for Selected 00- and PP- Pulps and a Kraft Reference Pulp

with an infinite number of plies is about the same for all of the pulps represented. Therefore, it could be argued that the density data in Table XVII rank handsheets in an acceptable way using the TAPPI method for thickness measurements.

TABLE XX

HANDSHEET THICKNESS DATA

Pulp	Beating Time, min.	Thickness per Sheet, μm. 5^a	∞^a	Difference, % (∞^a basis)
Kraft	0	101.4	98.3	3.2
00-2	1	99.4	95.9	3.8
PP-2	1	87.6	84.6	3.5
Kraft	10	85.3	83.0	2.8
00-2	14	83.9	81.4	3.1
PP-2	12	80.2	77.8	3.1

[a] Number of plies.

Acceptance assumes comparable "intermeshing" characteristics of handsheets from different pulps, but in Fig. 34 the shapes of the curves representing kraft compared with other pulps would seem to make this assumption questionable. If, in fact, differences in surface roughness cause variation in "intermeshing," measuring the thickness of samples by volume displacement of mercury should tend to eliminate surface roughness effects to give a more independent density (7).

The procedure for obtaining mercury pycnometric density as described in the experimental part is tedious and subject to error if air bubbles are trapped in the mercury. In this case, an apparently high caliper value is obtained. Table XXI includes all data recorded and discretion has been exercised in excluding values

TABLE XXI

TAPPI STANDARD AND MERCURY PYCNOMETRIC SHEET THICKNESSES AND SHEET DENSITIES

Pulp	Beating Time, min.	Caliper, μm. TAPPI[a]	Caliper, μm. Mercury[b]	Caliper, μm. Mercury, mean	Density, g./cc. TAPPI[c]	Density, g./cc. Mercury[d]	Density, g./cc. Mercury, mean	Operator	Density, TAPPI[e]
Kraft	0	100.1	85.1		0.608	0.709		a	0.596
			85.6			0.715			
			85.4	85.4		0.711	0.711		
Kraft	5	90.9	78.0		0.654	0.755		b	0.656
			77.0			0.765			
			76.9	77.3		0.774	0.765		
Kraft	10	83.9	70.2		0.702	0.837		a	0.695
			69.9			0.841			
			70.1	70.1		0.838	0.839		
Kraft	20	76.7	62.2		0.764	0.959		b	0.776
			64.0			0.932			
			62.0	62.7		0.952	0.948		
Kraft	35	71.1	63.8*		0.828	0.930*		b	0.845
			55.4			1.070			
			59.4*			0.971*			
		70.4	56.5		0.834	1.033		a	
			55.3			1.061			
			55.4	55.7		1.066	1.056		
00-1	10	107.4	73.7		0.538	0.767		b	0.541
			75.4			0.767			
			77.1	75.4		0.770	0.768		
00-1	30	96.3	73.5		0.611	0.787		b	0.611
			71.5			0.804			
			73.7			0.810			
		95.5	74.8		0.622	0.793		a	
			74.2			0.803			
			74.3	74.4		0.798	0.798		
00-1	41	88.6	66.5		0.668	0.901		b	0.681
			68.0			0.877			
			67.0	67.2		0.856	0.878		
00-2	1	98.0	68.8		0.616	0.860		b	0.608
			79.6*			0.751*			
			71.6			0.858			
		100.1	68.5		0.601	0.876		a	
			69.2			0.863			
			69.1			0.878			
		97.5	69.3		0.618	0.867		a	
			67.8			0.885			
			68.4	69.1		0.888	0.872		

[a] Mean of two determinations on 2 x 5 disks.

[b] Single disk values.

[c] Calculated from (a) and weight of ten disks.

[d] Calculated from (b) and weight of single disk.

[e] Value obtained when handsheets were originally tested for strength properties.

* Outlying result due in all probability to an air bubble trapped in the pycnometer and not included in mean value.

TABLE XXI (Contd.)

TAPPI STANDARD AND MERCURY PYCNOMETRIC SHEET THICKNESSES AND SHEET DENSITIES

Pulp	Beating Time, min.	Caliper, μm. TAPPI[a]	Caliper, μm. Mercury[b]	Caliper, μm. Mercury, mean	Density, g./cc. TAPPI[c]	Density, g./cc. Mercury[d]	Density, g./cc. Mercury, mean	Operator	Density, TAPPI[e]
00-2	14	84.1	62.5		0.726	0.975		a	0.731
			62.3			0.984			
			63.7	62.8		0.957	0.972		
00-2	18	85.3	65.4		0.771	1.025		b	0.778
			64.8			0.987			
			70.1*	65.1		0.939*	1.006		
PP-2	1	86.6	79.8*		0.711	0.743*		b	0.728
			60.0			0.941			
			73.5			0.906			
		87.6	64.9		0.696	0.940		a	
			65.6			0.925			
			65.7	65.9		0.933	0.929		
PP-2	12	79.8	60.3		0.762	1.007		a	0.774
			62.6			0.970			
			61.8	61.6		0.987	0.988		
PP-4	0	84.8	67.6		0.738	0.920		b	0.764
			66.0			0.928			
			67.9	67.2		0.925	0.924		
PP-4	7	77.7	60.0		0.774	0.991		b	0.785
			58.5			0.991			
			60.2	59.6		0.957	0.980		

[a] Mean of two determinations on 2 x 5 disks.

[b] Single disk values.

[c] Calculated from (a) and weight of ten disks.

[d] Calculated from (b) and weight of single disk.

[e] Value obtained when handsheets were originally tested for strength properties.

* Outlying result due in all probability to an air bubble trapped in the pycnometer and not included in mean value.

where it was judged a trapped air bubble was probably present. Accepted mean data were used in the plots shown in Fig. 35. If the curves for TAPPI sheet density versus mercury sheet density reflect no aging differences arising in the period during which handsheets were stored and there is no factor other than roughness involved, then TAPPI Standard T 220 m-60 does not form a satisfactory basis for determining handsheet density for comparing handsheet properties of a kraft with chlorine dioxide-alkali pulps, especially in the case of the OO- pulps.

Table XXII, derived from Fig. 35, shows the extent to which TAPPI handsheet density data for the kraft reference pulp and the chlorine dioxide-alkali pulps may diverge at the mercury sheet densities listed. It is an oversimplification to represent the OO- and PP- pulps as having the same TAPPI and mercury sheet density relationship. A reasonable expectation would be for the divergence away from the kraft pulp to be least for Pulp PP-4 and greater for Pulp OO-2, for example, which is the case. Thus, finer distinctions could be made, especially if more extensive information were to be obtained along the lines of that in Table XXI. It was decided not to pursue this course since there seems to be little doubt Table XXII serves to illustrate with sufficient discomfort the difficulty of using TAPPI handsheet density as a common parameter in comparing sheet properties of the chlorine dioxide-alkali and kraft pulps. Nevertheless, it is obvious from Table XXII that some reconsideration should be given to the data in Table XVIII where TAPPI handsheet densities were used as a common basis for comparison with a kraft pulp.

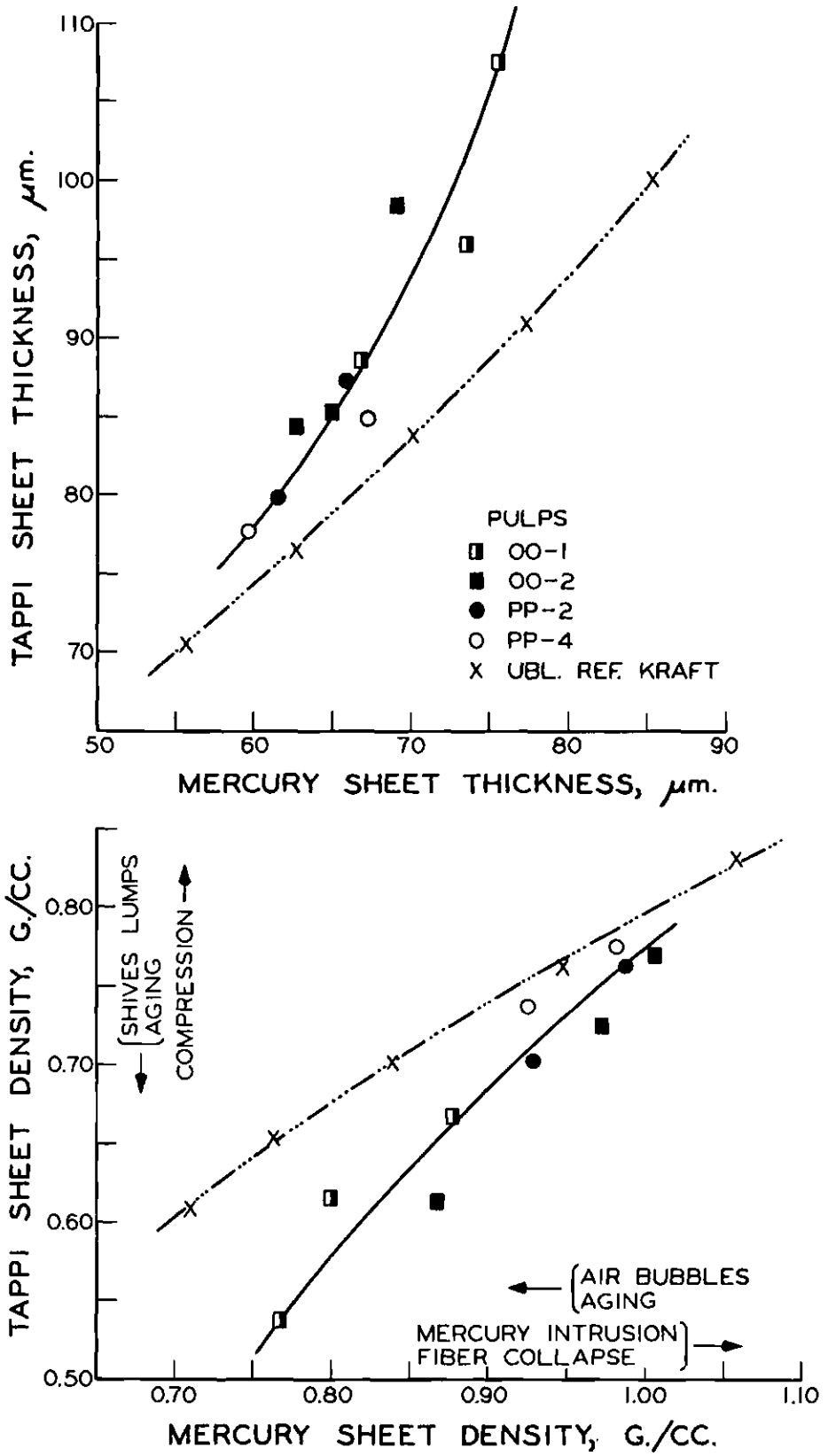

Figure 35. TAPPI Standard Method Versus the Mercury Displacement Procedure for Handsheet Thickness and Density for Selected OO- and PP- Pulps and a Kraft Reference Pulp

TABLE XXII

TAPPI HANDSHEET DENSITIES AT GIVEN MERCURY SHEET DENSITIES

Mercury, g./cc.	TAPPI Kraft, g./cc.	TAPPI OO- and PP- Pulps, g./cc.
0.69	--	--
0.76	0.65	0.53
0.82	0.69	0.60
0.92	0.75	0.70
1.01	0.80	0.78

To meet this desire handsheet data have now been assembled for comparison at the same "mercury" sheet density in Table XXIII. This puts the kraft pulp in the most favorable position at lowest handsheet density. However, depending on what combination is considered, it will be apparent the chlorine dioxide-alkali pulp properties not only vary appreciably with preparation procedures but also can compare well with the corresponding data for the kraft pulp at some sheet densities. Considering the appreciable difference in the yield of the kraft and chlorine dioxide-alkali pulps, the handsheet data obtained for the latter continue to appear favorable.

TABLE XXIII

COMPARISON OF HANDSHEET DATA AT THE SAME "MERCURY" DENSITY FOR CHLORINE DIOXIDE-ALKALI PULPS AND UNBLEACHED KRAFT PULP FROM ASPEN

Pulp	Kr.	00-1	00-3	Kr.	00-1	00-3	00-2	Kr.	00-1	00-3	00-2	00-4	PP-1	Kr.	00-2	00-4	PP-1	PP-2	PP-3	PP-4	Kr.
Mercury density, g./cc.	0.69[a]	——	0.76[b]	——	——	——	0.82[c]	——	——	——	——	0.92[d]	——	——	——	——	——	1.01[e]	——	——	——
TAPPI density, g./cc.	0.59	——	0.53	——	0.65	——	0.60	——	0.69	——	——	0.70	——	——	0.75	——	——	0.78	——	——	0.79	0.80
Canadian freeness, ml.	620	575	645	530	405	460	545	470	150	190	335	375	430	365	175	205	200	255	255	280	280
Beating time, min.	0[f]	7	0	5[f]	24	12	0	10[f]	48	30	10	1	3	17[f]	19	8	27	14.5	10	5	25[f]
Opacity, %	--	76	75	--	74	73	73	--	70	68	68	69	70	--	61	62	63	64	66	67	--
Breaking length, km.	5.4	5.5	5.1	7.1	7.6	7.3	6.4	8.2	9.9	9.8	9.1	9.0	7.1	9.5	10.7	10.7	9.8	9.4	9.2	9.2	10.4
Stretch, %	1.1	1.5	1.9	1.6	1.8	2.1	2.0	2.0	2.3	2.4	2.4	2.6	2.4	2.5	2.7	2.7	2.8	2.8	3.2	3.1	2.9
Tensile energy, abs., g.cm./cm.^{2}	26	32	42	50	58	64	54	66	88	92	88	97	74	90	117	116	122	108	124	117	112
Tensile stiffness, Et, kg./cm.	580	430	420	610	490	480	470	625	580	570	560	540	490	645	630	610	570	550	530	540	660
Burst factor	20	23	26	32	35	38	33	40	51	55	53	51	38	52	69	66	59	57	55	54	61
Tear factor (Elmen.)	57	52	59	69	48	54	59	74	42	45	52	56	57	74	47	52	50	50	56	50	69
Tear factor x yld./65	44	61	63	54	57	59	62	57	51	50	55	57	61	58	49	53	54	52	57	49	54
In-plane tear, g.cm./cm.	--	36	40	--	39	41	46	--	35	38	43	48	44	--	42	45	43	41	46	40	--
Zero-span breaking length, km.	20.4	14.3	14.3	20.6	16.1	16.1	14.5	20.5	18.2	18.2	17.6	16.9	15.5	20.3	19.5	19.8	18.7	17.6	18.0	16.4	20.0
Zero-span breaking lgth. x yield/65	15.7	17.0	15.9	16.0	19.1	17.8	15.2	16.0	21.2	20.0	18.5	17.1	16.6	15.7	20.8	20.3	20.6	18.2	18.1	15.8	15.5
z-dir. tensile, kg./cm.^{2}	--	6	4	--	11	10	10	--	20	20	19	19	16	--	30	28	29	29	26	30	--
M.I.T. fold	3	20	20	10	75	75	70	50	480	480	350	310	110	320	1090	1090	990	610	630	420	830

[a] All chlorine dioxide-alkali pulps outside relevant data.

[b] 00-2, 00-4, PP-1, PP-2, PP-3, and PP-4 outside relevant data.

[c] 00-4, PP-1, PP-2, PP-3, and PP-4 outside relevant data.

[d] PP-2, PP-3, and PP-4 outside relevant data.

[e] 00-1 and 00-3 outside relevant data.

[f] Valley beater bedplate load 5.5 kg. compared with 2.0 for the chlorine dioxide-alkali pulps.

HYDRODYNAMIC PROPERTIES OF SOME CHLORINE DIOXIDE-ALKALI PULPS

DISCUSSION

Introductory Comment

On some previous occasions (Report One, page 25; Report Three, page 59; Report Five, page 65, and in New York on February 22, 1968) reference has been made to the hydrodynamic properties of chlorine dioxide-alkali pulps, and there has been a question at times about hydrodynamic stability. The more extensive information now available will be considered.

Preliminary Data

As a convenient starting point, the hydrodynamic properties of various pulps are set out in Table XXIV. This reveals the marked increase that can occur in filtration resistance, specific surface, and specific volume when chlorited aspen holocellulose is extracted with alkali. The table also shows it is possible to obtain significantly different hydrodynamic properties in chlorine dioxide-alkali pulps, depending upon how they were prepared, which is as described in Reports Three and Six. One pulp, which had been bleached after mixing two unbleached pulps, had an initial Canadian freeness of 360 ml. that fell to 245 ml. after 5-min. circulation of the dilute stock in a Valley beater with no bedplate load, suggesting hydrodynamic instability. This same pulp also showed an unusual relationship to the unbleached materials in that hypochlorite bleaching caused the hydrodynamic properties to become more like those of a beaten pulp. Examples of beaten kraft pulps are included in the lower part of the table.

TABLE XXIV

HYDRODYNAMIC PROPERTIES OF VARIOUS PULPS

	Canadian Freeness, ml.	Filtration Resistance, at 10 cm. H_2O, $\underline{R} \times 10^{-8}$, cm./g.	Specific Surface, $\langle \bar{S}_w \rangle$, $cm.^2/g.$	Specific Volume, $\langle \bar{v} \rangle$, $cc./g.$
Chlorited aspen holocellulose	-	0.75	14,800	2.96
Previous aspen holopulp[a] [B(a)/VI-Perox.]	520	0.42	10,000	2.66
Previous aspen holopulp[a] [B(b)/VI-Perox.]	440	0.48	10,840	2.57
Present aspen holopulp[b] [LL-60]	565	0.85	14,300	3.01
Present aspen holopulp[b] [LL-240]	515	0.90	15,700	3.58
Bleached aspen holopulp[b] [LL-60/LL-240]	360[c]	1.74	21,700	3.35
Chlorited aspen holocellulose after alkali extraction	-	1.91	24,900	3.38
Bleached southern kraft, 70% hardwood-30% softwood, refined in Valley beater	450	1.97	21,200	3.10
Unbleached sycamore kraft refined in Valley beater	450	2.23	24,200	3.26

[a] Project 2500, Report Three.

[b] Project 2500, Report Six.

[c] Reduced to 245 ml. Canadian freeness by 5-min. circulation in Valley beater with no bedplate load.

Further Studies

To strengthen the knowledge available on hydrodynamic properties, further studies have covered the 00- pulps described in this report.

When these pulps were being beaten, drainage resistance data were obtained as detailed in the experimental part. For comparison, similar data were obtained on commercial unbleached and bleached aspen kraft pulps and on an unbleached laboratory-cooked aspen kraft. The Canadian freeness and corresponding average drainage resistance data presented in Table XXV are plotted in Fig. 36, from which the values in Table XXVI were obtained.

No endeavor has been made for the time being to seek an explanation of why the two curves in Fig. 36 are separated. However, the hydrodynamic properties of the 00- pulps plus the commercial unbleached and bleached aspen kraft pulps have been studied to provide information as presented in Table XXVII. With one exception, compressibility, specific volume, and specific surface data for the 00- pulps are about comparable to the data for kraft pulps. The exception is the compressibility of the 00- pulps beaten for 9 minutes. For the experimental conditions used, $\underline{N}$, for instance, is normally ≤ 0.400, although a value of 0.437 has been recorded for chlorited pulp from Douglas-fir springwood (8). The implication is that Pulp 00-4 tends to be more like a chlorited pulp, which is the case.

From a general viewpoint it appears reasonable to believe chlorine dioxide-alkali pulps with hydrodynamic properties approaching those of kraft pulps can be made.

TABLE XXV

CANADIAN FREENESS AND DRAINAGE RESISTANCE DATA

Pulp	Beating Time, min.	Canadian Freeness, ml.	Av. Drainage Resistance, $\underline{R} \times 10^{-8}$ cm./g.[a]
00-1	10[b]	545	0.622
	30	380	1.02
	38	245	1.92
	41	200	2.49
00-3	8[b]	500	0.762
	15	375	1.06
	24	270	1.72
	28	210	2.16
00-2	1[b]	525	0.660
	10	350	1.19
	14	275	1.63
	18	190	2.76
00-4	0[b]	400	0.926
	2	350	1.09
	5	275	1.48
	9	190	2.20
Commercial unbleached kraft	4[c]	527	0.733
	10	408	1.10
	14	336	1.44
	20	207	2.50
Commercial bleached kraft	2[c]	527	0.696
	6	485	0.874
	13	375	1.27
	20	245	1.94
	24	198	2.72
Laboratory unbleached kraft	12[c]	435	1.10
	28	190	3.02

[a] $\underline{\Delta P}$ = 10 cm. H_2O.

[b] Bedplate lever weight (Valley beater) = 2.0 kg.

[c] Bedplate lever weight (Valley beater) = 5.5 kg.

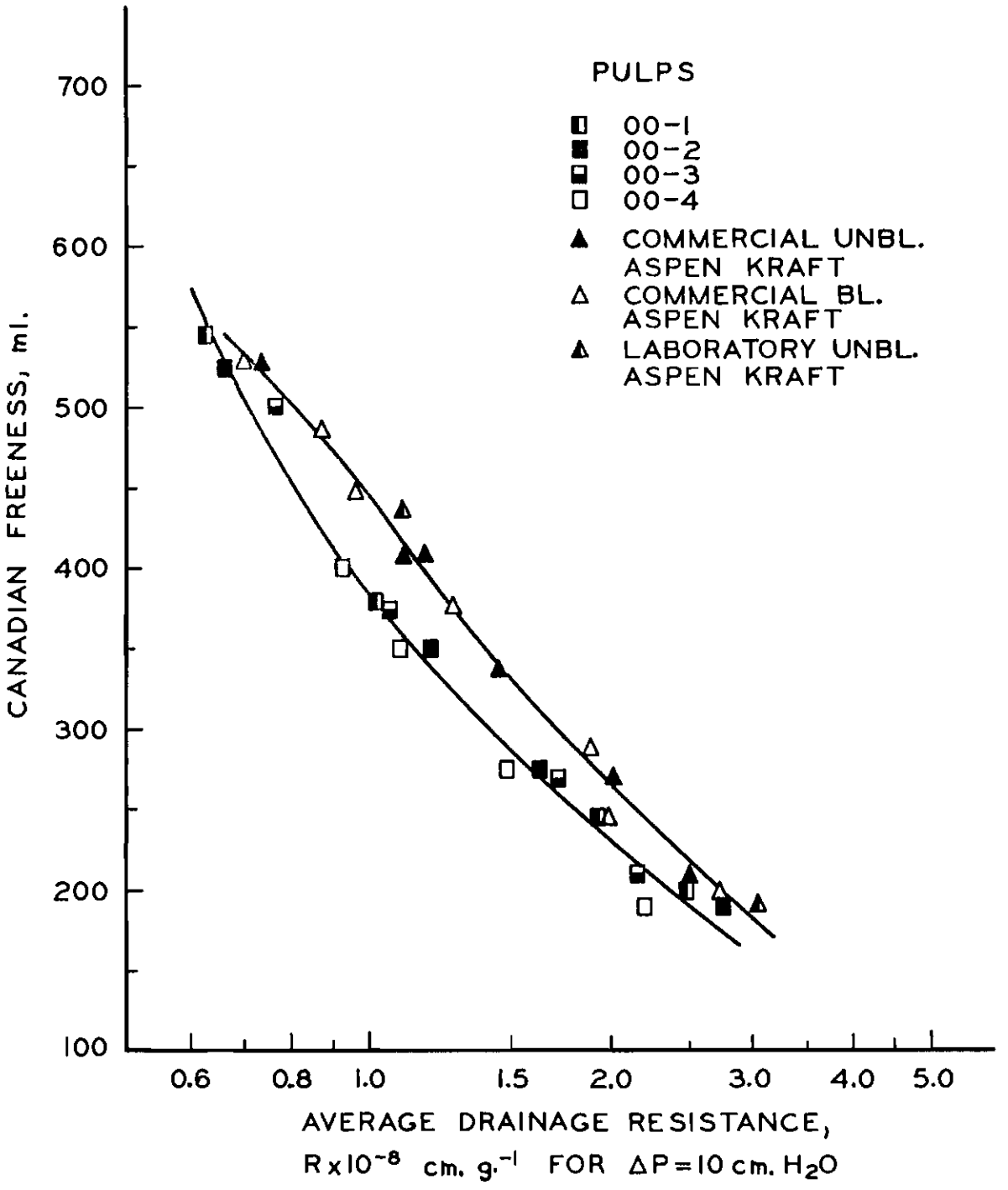

Figure 36. Relationship Between Canadian Freeness and Average Drainage Resistance of Pulps as Identified

TABLE XXVI

CANADIAN FREENESS AT CONSTANT DRAINAGE RESISTANCE

Kraft Pulps	00- Pulps	Drainage Resistance, $\underline{R} \times 10^{-8}$ cm. $g.^{-1}$, $\Delta\underline{P}$ = 10 cm.
500	450	0.81
400	345	1.16
300	260	1.72
200	175	2.72

TABLE XXVII

HYDRODYNAMIC PROPERTIES OF ASPEN PULPS

Pulp	Beating Time, min.	Canadian Freeness, ml.	$\underline{R} \times 10^{-8}$ cm./g. $\Delta\underline{P}$ = 10 cm. H_2O	Sp. Surface, $\langle\underline{S}_w\rangle$, $cm.^2/g.$	Sp. Volume, $\langle\underline{v}\rangle$, cc./g.	Compressibility, $\underline{c} = \underline{M}\underline{P}^{\underline{N}}$, $\underline{N}$	$\underline{M}^a$
00-1	30	380	1.02	17,700	3.18	0.388	0.00137
	41	200	2.49	30,300	3.26	0.388	0.00137
00-3	15	375	1.06	17,800	2.94	0.384	0.001655
	28	210	2.16	26,800	3.22	0.386	0.001655
00-2	10	350	1.19	19,100	3.12	0.386	0.001648
	18	190	2.76	31,300	3.40	0.405	0.00127
00-4	2	350	1.09	18,400	2.99	0.392	0.00156
	9	190	2.20	29,300	3.34	0.435	0.000914
Unbl. comml. aspen kraft							
Run 2	24	-	1.63	23,100	3.31	0.395	0.00138
	39	-	3.40	33,200	3.50	0.396	0.00144
Run 3	15	408	1.17	20,400	3.02	0.400	0.00129
	24	269	2.00	26,000	3.27	0.404	0.00125
Bl. comml. aspen kraft							
Run 1	17	-	1.52	21,200	3.04	0.383	0.001685
	28	-	3.11	30,800	3.27	0.383	0.001685
Run 2	8	446	0.967	17,200	2.92	0.390	0.00150
	18	288	1.80	23,900	3.19	0.390	0.00150

[a] $\underline{M}$, $g./(cc.)(dynes/cm.^2)^{\underline{N}}$.

EXPERIMENTAL

RAW MATERIALS

Chip Lot A3/55 was used for the OO- and PP-coded series of experiments.

Unscreened fiberized chips were prepared according to the procedure in Report Three, page 55, except that a more even feed rate was used as referred to in Report Six, page 48.

ALKALI CONDITIONING

The preliminary alkali conditioning at 50°C. with 3.0% sodium hydroxide was carried out for 60 min. at 6.0% consistency in 10 in. x 20-in. 0.002-in. cal. high-density polyethylene bags* using 500-g. lots of fiberized chips. Extracted fiberized chips were filtered on a fritted-glass funnel, washed with about 2.5 liters of tap water at near 50°C., then with cold tap water (3-4 x 2.5 liters) and the free water removed without difficulty from the fibrous pad by suction.

CHLORINE DIOXIDE REACTION

The reaction with aqueous chlorine dioxide (9.0%) was carried out directly after chip fiberization in the OO- series, for example, in 10-gal. polyethylene carboys using 1575-g. lots of fiberized chips at 5.0% consistency. Approximately half of the 3.5% sodium hydroxide buffer was added to the pulp and the remainder was added to the aqueous chlorine dioxide (resultant pH = 6.0-6.5) just prior to its addition to the fibrous suspension. The reaction mixture in the carboy was brought to 35°C. in about 45 min. by immersion in a constant-temperature bath with shaking from time to time. After exhaustion of the oxidant, the fibrous product

---

* Tower Packaging Co., 1150 S. Willis Ave., Wheeling, Ill. 60090.

was collected in a nylon-bag-lined centrifuge and following removal of the mother liquor the pulp was washed with tap water by reslurrying in the bag. The water was removed by centrifuging and this washing procedure repeated about three times. No significant resistance to drainage was observed.

ALKALI EXTRACTION

The alkali extractions of PP-II, for example, were carried out using high-density polyethylene bags, as specified above, containing 200 g. o.d. fiber. After extraction under the conditions as tabulated, the fibrous products were collected on a fritted-glass funnel and washed first with about 2.5 liters of tap water at 60°C. and then with cold water (3-4 x 2.5 liters). It was progressively more difficult to filter the pulps when the extraction time was greater. For the PP-coded treatments set out in Table I, the pulp at this stage was screened on a flat-bed 0.006-in. cut screen with the accepts collected on a muslin-covered washbox. The accepts were dewatered in a nylon-bag-lined centrifuge and then held for hypochlorite bleaching. For the other PP- and OO-coded pulps where Valley beater runs and handsheet evaluations were carried out, the products at this stage were not screened and were collected on fritted-glass funnels.

HYPOCHLORITE REACTION

The hypochlorite reactions on the PP-III-coded pulps, for example, were carried out in standard polyethylene bags (6 in. x 8.5 in. with 20 g. o.d. pulp) using the conditions as tabulated. The pulps were collected on a sintered-glass funnel, washed with cold distilled water 3 x approx. 500 ml.), soaked in approx. 500 ml. of sulfurous acid (pH 3.5-4.0) for 30 min., dewatered, and washed again as before.

Each pulp was more difficult to filter than before bleaching, and the pulps reacted with increased amounts of hypochlorite were progressively harder to filter. Thus the most difficult pulp to filter was PP-III 120 after reaction with 4.5% available chlorine.

Brightness handsheets were made according to TAPPI T 218 m-59. Brightness determinations were carried out the following morning before and after aging the handsheets at 105°C. for 60 min.

PULP EVALUATION

Pulp beatings were carried out in a 1-1/2 lb. Valley beater according to TAPPI Standard Method T 200 ts-66 but using a 2.0-kg. weight on the end of the bedplate lever and withdrawing 1600 ml. of stock at each beating interval. Canadian freeness determinations were made as set out in TAPPI Standard Method T 227 m-58. Handsheets were formed as in TAPPI Standard Method T 205 m-58, ten 60-g./m.^{2}, one 50-g./m.^{2}, and one 120-g./m.^{2} handsheets being formed at each beating interval. The following tests were carried out on the nominal 60-g./m.^{2} handsheets:

Opacity, %	TAPPI Standard Method T 425 m-60.
Density, g./cm.^{2}	TAPPI Standard Method T 220 m-60.
Breaking length, km.	
Stretch, %	
Burst factor	
Tear factor	
M.I.T. fold	
Tensile energy absorption, g. cm./cm.^{2}	TAPPI Standard Method T 494 su-64.
Tensile stiffness, E.t., kg./cm.	Calculated from the slope of the initial load/elongation curve determined for the tensile energy absorption tests.

In-plane tear, g. cm./cm. (9).

For the last three tests the results were corrected to a 60-g./m.^{2} basis weight by sample proportion.

For all tensile testing, i.e., breaking length, stretch, tensile energy absorption, and tensile stiffness, a table-model Instron tester was used. The jaw separation was 4.0 in., the test piece width 1.00 in., and the crosshead speed was 1 in./min.

Zero-span breaking length tests were carried out on the 50-g./m.^{2} handsheets essentially according to TAPPI Standard Method T 231 sm-60.

The 120-g./m.^{2} handsheets were used for the z-direction tensile test (10).

MERCURY PYCNOMETRIC MEASUREMENTS

The procedure for comparing the mercury pycnometric caliper and density with the TAPPI caliper and density was as follows: From a set of handsheets 10 disks, each 2.896 cm.^{2} in area, were punched out and weighed. Two TAPPI thickness measurements were then made. Three of the disks, selected at random, were separately weighed and then placed in a small pycnometer with the mercury displaced being measured after careful evacuation (see TAPPI Routine Control Method 256).

HYDRODYNAMIC EVALUATION

Drainage resistance measurements were made with a Cutler-Hammer, A.I.L. Division, Type 273 Drainage Resistance Analyzer. The unit has a 20-liter Lucite deckle and a 3-in. diameter septum with a 64 x 51-mesh nylon screen. A centrifugal pump with a needle valve throttle on the output followed by a rotameter (91 ml./sec. maximum) is used to obtain a constant flow rate past the septum. Transducers located on either side of the septum provide a measure of the pressure drop (up to

100 cm. water) across the fiber mat as it forms and this is recorded on a strip chart as a function of time. The water temperature during a test is indicated by a thermometer located downstream from the pump. The water supply was Appleton city water filtered by one Commercial Filters, Boston, unit. Further information on the Analyzer can be obtained from Cutler-Hammer, Inc., Deer Park, L. I., New York 11729.

The pulp consistency in the deckle was fixed at 0.1 g. (o.d.)/liter and manual agitation using a perforated 3-in. diameter sheet mold stirrer was maintained throughout each run. The flow rate which was held constant during each run was chosen to give a run time of 90-120 sec. for a pressure build-up of 90 cm. water. Generally, three runs were made at each beating interval using a fresh sample of pulp for each run. Drainage resistance was calculated as follows:

$$\text{Drainage resistance, } R \times 10^{-8} = \frac{A^2 \Delta P}{C\mu q^2 \theta} \text{ cm./g.}$$

$$= \frac{2.03 \times 10^5 \Delta P}{\mu q^2 \theta} \text{ cm./g.}$$

where

$\underline{A}$ = area of septum, cm.^{2},

$\Delta \underline{P}$ = pressure drop across fiber mat on septum, cm. water,

$\underline{C}$ = fiber consistency in deckle, g./cc.,

μ = water viscosity, poises(dyne-sec./cm.),

$\underline{q}$ = flow rate through fiber mat, cc./sec., and

θ = time, sec.

A typical example of drainage resistance data obtained for the pulps studied is shown in Table XXVIII for the case of one pulp, namely, 00-3.

TABLE XXVIII

DRAINAGE RESISTANCE DATA FOR PULP 00-3

Beating Interval, min.	Canadian Freeness,[a] ml.	Flow Rate, cc./sec.	ΔP, cm. H_2O	Drainage Resistance, $R \times 10^{-8}$, cm./g. Run 1	2	3	4	Mean
8	500	81.4	10	0.705	0.761	0.745		0.737
			20	1.00	1.08	1.06		1.05
			30	1.27	1.35	1.33		1.32
			40	1.55	1.58	1.57		1.57
			50	1.78	1.79	1.79		1.79
			60	1.99	2.00	2.00		2.00
			70	2.20	2.21	2.20		2.20
			80	2.40	2.40	2.39		2.40
			90	2.57	2.56	2.56		2.56
15	375	62.8	10	1.05	1.06	1.08		1.06
			20	1.51	1.50	1.54		1.52
			30	1.89	1.86	1.93		1.89
			40	2.24	2.18	2.28		2.23
			50	2.57	2.50	2.61		2.56
			60	2.87	2.79	2.92		2.86
			70	3.16	3.07	3.22		3.15
			80	3.43	3.33	3.50		3.42
			90	3.70	3.57	3.76		3.68
24	270	44.8	10	1.78	1.71	1.67		1.72
			20	2.63	2.55	2.49		2.56
			30	3.33	3.25	3.17		3.25
			40	3.97	3.92	3.81		3.90
			50	4.57	4.51	4.42		4.50
			60	5.13	5.09	4.98		5.07
			70	5.69	5.67	5.53		5.63
			80	6.21	6.21	6.05		6.16
			90	6.73	6.67	6.53		6.64
28	210	44.8	10	2.10	2.10	2.28	2.14	2.16
			20	3.16	3.15	3.31	3.22	3.21
			30	4.08	4.06	4.17	4.06	4.09
			40	4.93	4.87	4.97	4.95	4.93
			50	5.69	5.63	5.75	5.70	5.69
			60	6.42	6.37	6.46	6.45	6.42
			70	7.12	7.07	7.16	7.19	7.14
			80	7.83	7.75	7.82	7.88	7.82
			90	8.46	8.37	8.42	8.50	8.44

[a] Single freeness determination at each beating interval.

The specific surface and specific volume data were obtained by measuring the compressibility of the fiber mat in an aqueous suspension under increasing static loads and using the constant, $B = A^2\rho g/C\mu q^2$, from the drainage resistance equation. A full description of the fiber compressibility apparatus and a mathematical treatment on this subject is given by Han (11).

ACKNOWLEDGMENTS

The authors are grateful for the assistance and encouragement provided by other members of the Institute, particularly B. D. Andrews, E. A. Cary, S. T. Han, J. D. Hankey, J. R. Taggart, V. J. Van Drunen, R. P. Whitney, and the Paper Evaluation personnel. The ultraviolet and infrared spectra data reported in Appendix I were obtained by M. A. Buchanan with assistance from L. O. Sell and H. F. Hanel.

LITERATURE CITED

1. Watson, A. J., and Phillips, F. H., Appita 16, no. 6:165(1963).

2. Rys, L. J., Pulp Paper Mag. Can. 65:T-25(Jan., 1964).

3. Watson, A. J., Appita 14, no. 4:144(1961).

4. Browning, B. L., and Wink, W. A., Tappi 51, no. 4:156(1968).

5. Liebergott, N., and Yorston, F. H., Tappi 48, no. 1:20(1965).

6. Dean, J. C., Saul, C. M., and Turner, C. H., Appita 22, no. 1:30(1968).

7. Taylor, D. L., Tappi 47, no. 7:165A(1964).

8. Han, S. T. The status of the sheet-forming process. A critical review. p. 151. Appleton, Wis., The Institute of Paper Chemistry, Dec. 31, 1965.

9. Van den Akker, J. A., Wink, W. A., and Van Eperen, R. H., Tappi 50, no. 9: 466-70(1967).

10. Wink, W. A., and Van Eperen, R. H., Tappi 50, no. 8:393(1967).

11. Han, S. T. The status of the sheet-forming process. A critical review. p. 129-154. Appleton, Wis., The Institute of Paper Chemistry, Dec. 31, 1965.

12. Busche, L. R. The Klason lignin determination as applied to aspenwood with special reference to acid-soluble lignin. Doctoral Dissertation. Appleton, Wis., The Institute of Paper Chemistry, 1960; Tappi 47, no. 12:808-11(1964).

13. Pilipchuk, Y. S., Pen, R. Z., and Finkelstein, A. V., Lesnoi Zh. 11, no. 4: 167(1968); A.B.I.P.C. 39:7516(1969).

THE INSTITUTE OF PAPER CHEMISTRY

R. G. Jamieson
Research Fellow

G. A. Nicholls
Senior Research Associate

Division of Materials Engineering & Processes

APPENDIX I

ULTRAVIOLET AND INFRARED SPECTRA OF MODIFIED LIGNINS[1]

Spectra absorptivities were presented in Progress Report Two for various lignin preparations isolated after reacting aspenwood with acidified chlorite. Although the spectra were somewhat similar to the spectra of milled wood lignin from aspenwood, they indicated that appreciable degradation had occurred during the chlorite treatment. The spectra varied from one preparation to another, and thus they seemed to offer little promise for the quantitative estimation of the modified lignin.

Later, modified lignins were isolated after reacting fiberized aspenwood with three levels of chlorine dioxide as described in Progress Report Four, but at the time it did not seem worthwhile to determine the spectra of these lignins. However, since these lignins are more representative of the lignins formed in holopulping, it recently seemed desirable to determine their spectra.

Ultraviolet spectra for five modified lignins are given in Fig. 37 along with the spectrum of Milled Wood Lignin A which had been determined by Busche (12). The spectrum of the lignin isolated from wood treated with 9% chlorine dioxide is not shown because it was close to Curve C. It was slightly higher below 200 nm., but somewhat lower above 240 nm. Spectra for the modified lignins were determined on 75% ethanol solutions using the Carey Model 15 Spectrophotometer, whereas that for the milled wood lignin was for a methyl cellosolve solution using a Beckman DK-2 Spectrophotometer. Busche reported that the maximum of lignin preparations was shifted to 209.5 nm. in aqueous methyl cellosolve solutions. Since the milled wood lignin contained 9% carbohydrate material, the absorptivity of the original

---

[1] The term "hololignins" was used in previous reports. The use of this term has been discontinued because "holo" signifies "entire."

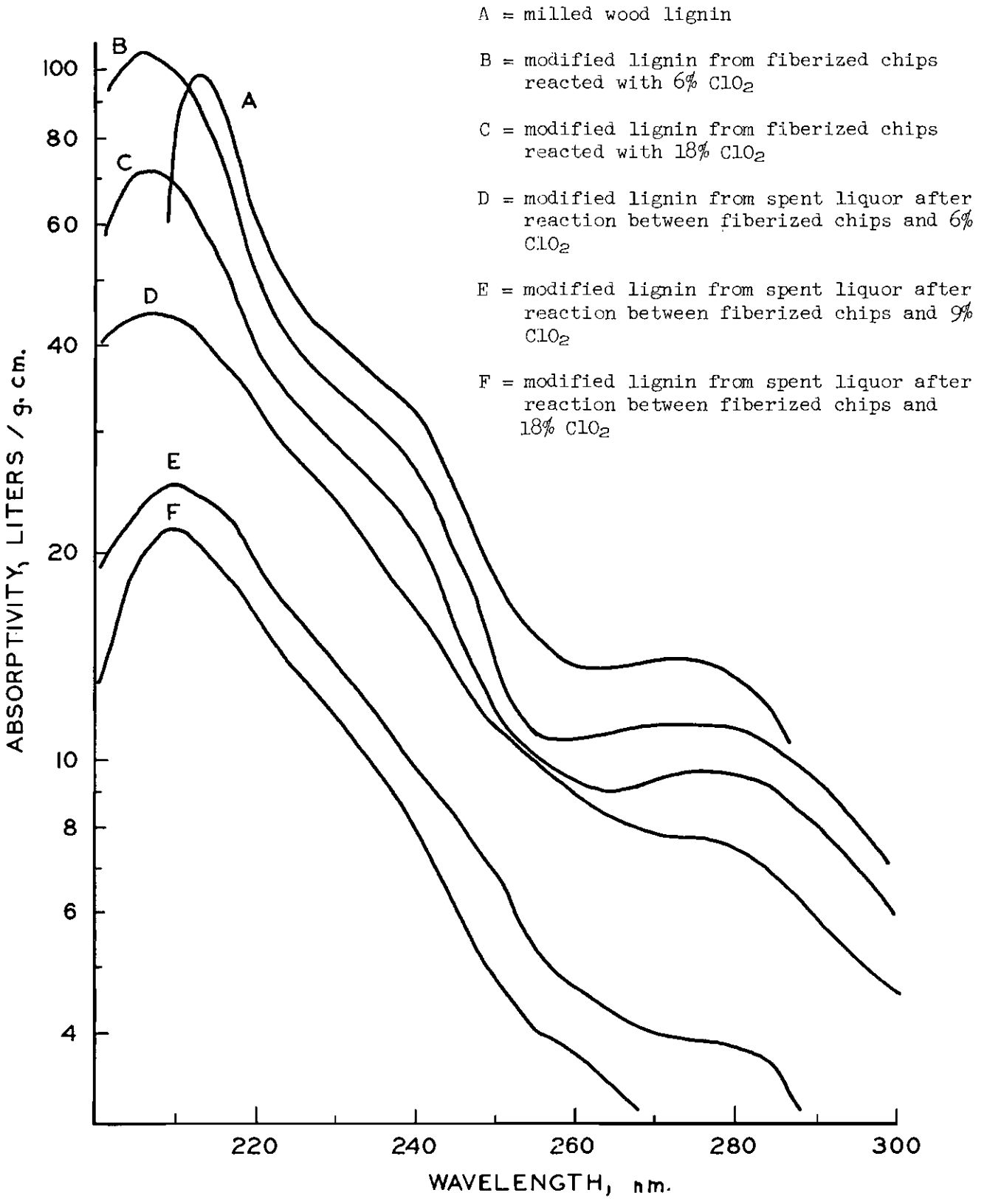

Figure 37. Ultraviolet Spectra of Lignin

aspen lignin presumably is about 10% higher than indicated by Curve A in Fig. 37. Thus, all of the modified lignins have less absorptivity in the ultraviolet region than does the original lignin. This may be due in part to the introduction of chlorine, but the major loss in absorptivity is believed to be due to loss of aromatic groups.

The spectra in Fig. 37 indicate an increase in lignin degradation as the amount of chlorine dioxide was increased from 6 to 18%, and also that the lignins isolated from the spent liquors were degraded much more than those isolated from the reacted wood.

Calculated "C-9 unit weights" were given in Table VI of Progress Report Four for the two lignins isolated from the 9% chlorine dioxide reaction and for milled wood lignin. Comparison of absorptivities based on these units provides a means of eliminating the effect of addition of chlorine and oxygen during the original reaction. Such a comparison is made in Fig. 38.

Infrared spectra for the six modified lignins were run on a Perkin Elmer Model 621 Grating Infrared Spectrophotometer using the potassium bromide technique, and four spectra are given in Fig. 39. The lignins isolated from the three reacted woods showed strong bands at 1760, 3420, 2940, 1325, and 1580/1500 $cm.^{-1}$ indicating the presence of carbonyl, hydroxyl, aliphatic carbon-hydrogen, methoxyl (13), and aromatic groups, respectively. As the amount of chlorine dioxide used was increased from 6 to 18% there apparently is an increase in carbonyl and decrease in aromatic groups in the resulting lignins.

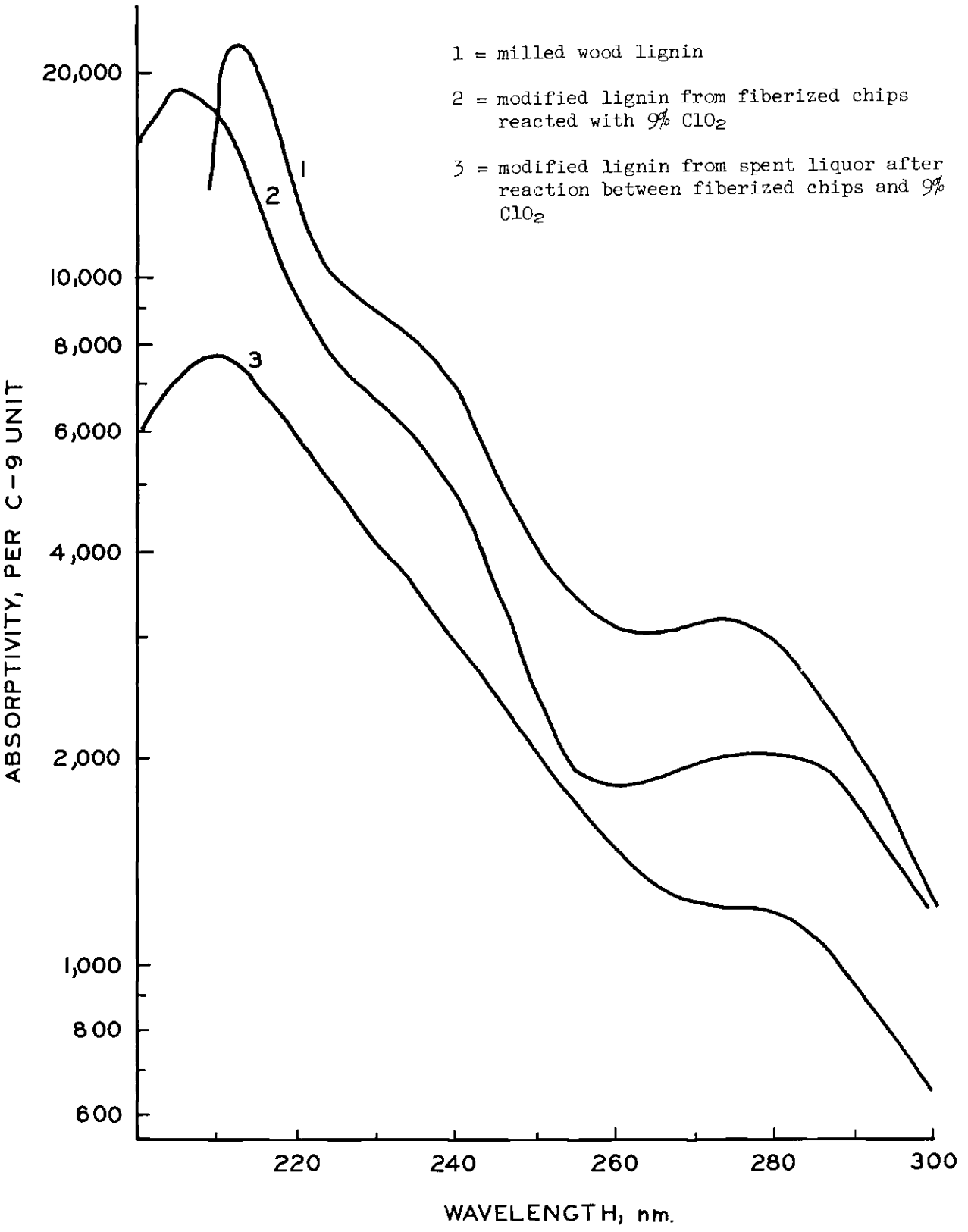

Figure 38. Ultraviolet Spectra of Lignin

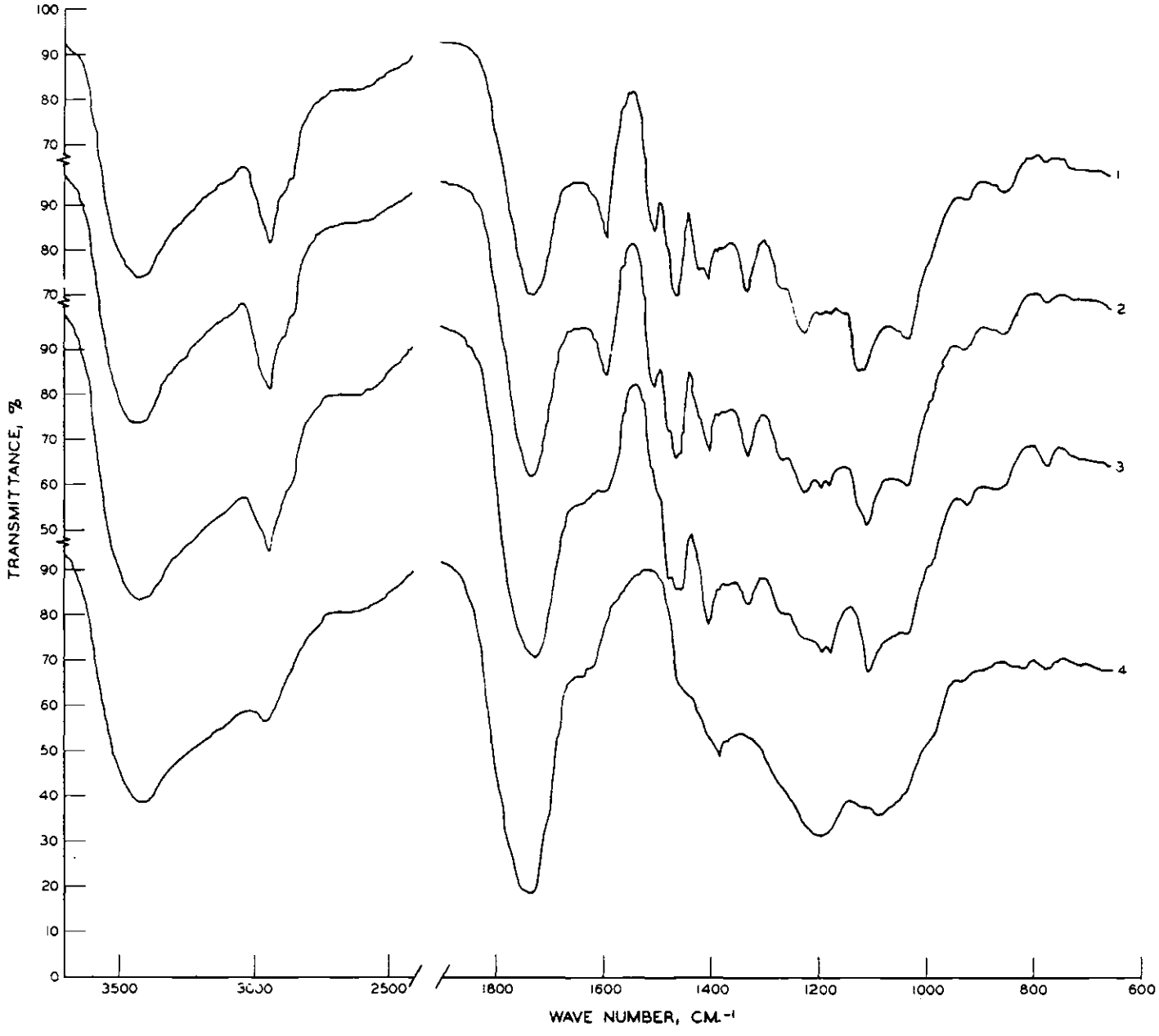

Figure 39. Infrared Spectra of Modified Lignin from Fiberized Chips Reacted with (1) 6%, (2) 9%, and (3) 18% ClO_2, and (4) from Spent Liquor After Reaction Between Fiberized Chips and 9% ClO_2

The infrared spectra for the three lignins isolated from the spent liquors were nearly identical. All showed broad, poorly resolved bands due to carbonyl, hydroxyl, and aliphatic carbon-hydrogen groups. There was no indication of aromatic groups in these spectra.